Investigation of the Deformation and Recovery Behavior of Nylon-6/Rubber Thermoplastic Vulcanizates on the Molecular Level by Infrared-Strain Recovery Measurements

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Received April 13, 2001

ABSTRACT: Thermoplastic vulcanizates (TPVs) prepared by dynamic vulcanization are blends in which cross-linked rubber particles are finely dispersed in a thermoplastic matrix. These blend materials, which are in our case based on nylon-6 and EPDM rubber, show excellent strain recovery behavior, even though the matrix consists of a semicrystalline polymer which should deform plastically. To understand the elastic behavior, infrared spectroscopy in combination with tensile stress−strain measurements have been used. With this method it was possible to follow the orientation behavior of the different phases during stretching. It could be shown that for blends with a high content of rubber (≥60 wt %) the degree of orientation of the crystalline and amorphous phase in the nylon matrix is much smaller compared to that of pure nylon during deformation, while the EPDM rubber phase is almost completely stretched. This fact can only be accounted for by a model that assumes a very inhomogeneous phase deformation of the nylon matrix and a good adhesion between the matrix and the dispersed rubber particles. The plastic deformation will be initiated and concentrated in zones where the matrix ligaments are thinnest, whereas the thicker nylon ligaments remain unyielded.

1. Introduction

Thermoplastic vulcanizates (TPVs) are blends of a thermoplastic polymer and a cross-linked synthetic rubber. The rubber is dynamically cross-linked during melt-blending. Because of this procedure, it is possible to disperse a high amount of rubber in the thermoplastic matrix.[1] In a previous paper,[2] we discussed the way to disperse a high amount of rubber in an engineering plastic, despite the high interfacial tension between the two polymer components. By a careful selection of the viscosity ratio between the rubber and the nylon, combined with the use of a suitable compatibilizer and cross-linking agent, it was possible to disperse up to 60 wt % of rubber in the nylon matrix. The continuous nylon phase provides these blends with important properties such as melt processability and a good heat and solvent resistance. These nylon/rubber TPVs also exhibit excellent elastic properties. In this paper we investigate the deformation and recovery behavior of the different phases in these materials in order to get a thorough understanding of the elastic behavior of these blend materials.

The elastic behavior of TPVs cannot be understood only from the blend morphology. The continuous phase, being a semicrystalline polymer, is only elastic when the applied deformation remains small (15−20% strain). There will be almost no recovery after the yield strain is passed. One would expect that the deformation behavior of a TPV is similar to that of its continuous phase. However, these materials display a high elasticity although the matrix phase consists of a thermoplastic polymer which is expected to deform plastically.

Several models have been used in the literature to describe the deformation behavior of TPVs, especially for PP/EPDM blends. Kikuchi et al.[3,4] used finite element analysis on a two-dimensional model of particles in a matrix. These authors predicted that at least 70% of the PP matrix is deformed beyond its yield point when the material is stretched; the rest of the PP matrix would act as a glue between the rubber particles. They assume that these rigid adhesion points provide the elastic behavior of TPVs. The reason why it is possible to pull back such large amount of plastically deformed matrix material by the elastic forces of the rubber is not explained.

Kawabata et al.[5] suggested a three-dimensional model of rubber particles in a thermoplastic matrix. The adhesion between the rubber particles and the matrix was assumed to be very weak apart from a few points on the interface, so that a large amount of voids is formed when the TPV is deformed. As in the theory of Kikuchi et al.,[3,4] it is proposed that these “adhesion point” link the rubber particles together in a continuous network, and this leads to the macroscopically observed elastomeric behavior. How it is possible that, on the same particle−matrix interface, both adhesion and debonding can occur is not explained, especially not for TPV systems were the adhesion between the rubber and the matrix is known to be very good, like PP/EPDM.

Yang et al.[6] used WAXD analysis to investigate the crystal orientation of the polypropylene matrix during stretching and relaxation. They found that the degree of orientation of the crystalline phase of the PP in the TPVs after deformation is almost half compared to that of pure polypropylene. After relaxation, a large degree of crystalline orientation still remains in the polypropylene phase. This implies that even when there is a

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10.1021/ma010651v CCC: $22.00

certain degree of crystalline orientation, the material still can display a high degree of elasticity. Soliman et al.[7] used infrared spectroscopy in combination with tensile stress−strain measurements to measure in situ the orientation of the different phases. They found that the whole EPDM rubber phase is stretched during deformation, while only a very small fraction of the polypropylene matrix is deformed; it is assumed that the plastic deformation of the PP phase is localized at the boundary between different rubber particles.

The present paper describes the deformation behavior of nylon/rubber TPVs at the molecular level by rheooptical Fourier transform infrared-strain recovery measurements. Using this method, it will be possible to get a better understanding of the elastic properties of a nylon/rubber TPV. The influence of the rubber content, the temperature, and the applied strain on the orientation behavior of the different phases will be examined in detail.

2. Experimental Section

2.1. Materials. For the blend systems studied in this work a low/medium high molecular weight nylon-6 was used ($M_w \approx$ 25 000 kg/kmol, $\rho = 1.14$ g/mL). The nylon (trade name Akulon k123) was kindly supplied by DSM.

For the rubber phase two different modified EPDM rubbers were used, both having a high molecular weight ($\rho = 0.88$ g/mL). The two EPDM rubbers differ in the ethylene−propylene ratio: 75/25 and 50/50 wt %. The two modified EPDM rubbers that were used are a maleic anhydride (MA) modified ethylene−propylene (75/25 wt %) copolymer (0.5 wt % MA), type Royaltuf 465A, and a maleic anhydride (MA) modified ethylene−propylene (50/50 wt %) copolymer (1 wt % MA), type Royaltuf 465. These rubbers were kindly supplied by Uniroyal.

2.2. Blend/Sample Preparation. Prior to the melt-mixing operations, all materials were dried under vacuum at 120 °C overnight. The components were then melt-mixed and dynamically vulcanized in a mini-extruder (DSM Research, The Netherlands), which is a conical corotating fully intermeshing twin-screw extruder, with a capacity of about 4 cm^3. A recirculation channel allows to vary the blending time. All blends were prepared under nitrogen atmosphere to prevent oxidative degradation. The components were melt-blended for 6 min at a screw speed of 80 rpm and a temperature of 260 °C. The peroxide (0.25 wt %) was first dissolved in mineral oil and afterward premixed with the rubber in a Haake 69 cm^3 batch kneader before the nylon/rubber blend was compounded. The peroxide was dissolved in mineral oil (2 wt %) to achieve a better dispersion of the peroxide in the rubber.

The samples for IR investigation should be around 30 μm thick. To meet this requirement, an extruded strand of the blend was placed between two Teflon sheets and compression-molded at a temperature of 250 °C. Afterward, the film was cooled until room temperature with cold water. From the molded films samples were cut with a length of 20 mm and a width of 6 mm. A film thickness of 30 μm was chosen, because in the case of a larger thickness the IR absorption peak of the amorphous phase of the nylon (see section 2.4) showed too much over-absorption.

2.3. Morphological Analysis. The phase morphology of the blends was examined on the extruded strands (perpendicular to the extrusion direction) with a transmission electron microscope (TEM), Philips XM10. To examine the phase morphology by TEM, slices of 80 nm were cut with a diamond knife, using a Leica Ultracut ULT microtome, equipped with a liquid nitrogen cooling unit. The specimen temperature during microtoming was −100 °C and the knife temperature −55 °C. The samples were stained with an OsO_4/formaldehyde solution.

2.4. Infrared-Strain Experiments. Infrared-strain experiments, also known as rheooptical experiments in the literature,[8] combine a tensile test with infrared chain orientation measurements, showing how the applied strain is divided across the different phases in the sample. The more a phase is deformed, the more its molecular chains will be oriented in the direction of strain. Chain orientation is not the only information that can be obtained with this method; also, crystallization and phase transitions during strain can be observed. Strain-induced crystallization can be observed when the total amount of absorbed light for a certain peak changes or a new peak appears. Phase transitions during strain can be observed when some specific phase infrared absorption peaks appear during stretching and others disappear.

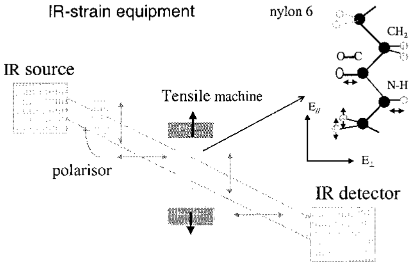

Figure 1. Experimental setup for infrared-strain measurements.

2.4.1. IR Orientation Measurements. Theoretical Aspects. Infrared light of specific frequencies can be absorbed by chemical groups in the polymer material. The frequency of infrared absorption is determined not only by the kind of chemical group and its vibrational mode but also by its surroundings (crystalline or amorphous) and mechanical stresses. The absorption is dependent on the angle between the transition moment vector of the vibration and the electric field vector of the light. For a given mode of vibration the transition moment vector has a specific orientation in the molecule. If polarized light is used, the absorption is directly related to the distribution of the transition moment vectors in the material. This means that if the polymer chains in a sample are oriented, the level of absorption of polarized light will be dependent on the polarization direction. To determine the chain orientation in a sample with infrared spectroscopy, the dichroic ratio is used,[8−10] which is defined as

$$R = \frac{A_{\|}}{A_{\perp}} \tag{1}$$

where $A_{\|}$ is the absorption of light polarized in the stress direction and $A_{\perp}$ is the absorption of light polarized in the perpendicular direction. For the orientation measurements the polarization direction of the incident radiation is alternately adjusted parallel (||) and perpendicular (⊥) to the stretching direction at the end of each scan (see Figure 1).[11]

The chain orientation can be expressed by an orientation function (f) calculated with the IR dichroic ratio[8−10]

$$f = \frac{(R-1)(R_o+2)}{(R+2)(R_o-1)} \tag{2}$$

where R is the dichroic ratio and R_o is the dichroic ratio of a perfectly oriented sample. In the most simple situation, the chain axes are perfectly aligned with the direction of stretching, and the transition moment vectors have a distribution that is rotational symmetrical around the chain axis.[8−10] In this case the dichroic ratio will be given by

$$R_o = 2\cot^2\theta \tag{3}$$

where θ is the angle between the transition moment vector **M** and the chain axis. If the transition moment vector of the molecular vibrations is directed either parallel ($R_o = \infty$) or perpendicular ($R_o = 0$) to the chain axis, the orientation

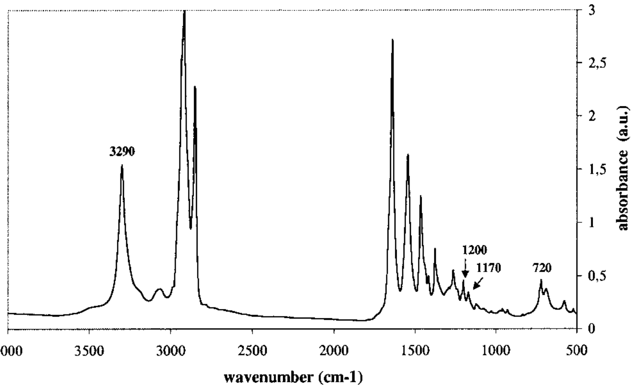

Figure 2. Infrared spectrum of a nylon-6/EPDM-*g*-MA (40/60 wt %) TPV.

Table 1. IR Absorption Peaks of a Nylon-6/EPDM TPV

wavenumber (cm^{-1})	vibrational mode	phase
720	CH_2 rocking	crystalline EPDM
1170	CH_2 twist-wagging	amorphous PA6
1200	CH_2 twist-wagging	crystalline PA6

function (eq 2) reduces respectively to

$$f_{\parallel} = \frac{R-1}{R+2} \tag{4}$$

$$f_{\perp} = \frac{-2(R-1)}{R+2} \tag{5}$$

2.4.2. Infrared Spectrum of a Nylon-6/EPDM-*g*-MA Blend or TPV. The IR absorption peaks[12-15] used in this investigation can be found in Table 1. In Figure 2 a static spectrum of a nylon-6/EPDM-*g*-MA (40/60 wt %) TPV at room temperature is shown.

The vibration of crystalline EPDM is perpendicular to the chain axis (see Figure 1). Under the assumption that the transition moment directions for both vibrations make an angle of 90° with the polymer chain axis, the corresponding orientation function is represented by eq 5. The vibrations of crystalline and amorphous nylon-6 (CH_2 twist-wagging) are parallel to the chain axis (see Figure 1). Under the assumption that the transition moment directions for both vibrations make an angle of 0° with the polymer chain axis, the corresponding orientation function is represented by eq 4.

2.4.3. IR-Strain Recovery Measurements. The equipment to perform IR-strain recovery measurements (see Figure 1) was composed of a Fourier transform infrared spectrometer (Bruker IFS66) with a liquid nitrogen cooled infrared detector and a ministretching device (FSK, load cell = 100 N). The strain recovery tests were done in situ with infrared spectroscopy. The sample was first stretched at a constant strain rate to a certain strain. Then the strain was reversed while the strain rate remained the same, until zero stress was reached.

The samples were stretched at a constant rate (20%/min) for 5 min (100% strain). With the polarized radiation, it was possible to obtain alternating spectra. The direction of polarization was changed 90° after the recording of each spectrum. Each measurement resulted in 60 spectra: 30 spectra during elongation and 30 spectra during recovery. From these spectra the height of the absorption peaks was determined by fitting the peaks with a Lorentz-shaped peak. From the ratio in peak height, the dichroic ratio (*R*) was determined.

3. Results and Discussion

3.1. Influence of the Rubber Content on the Deformation and Recovery Behavior. The influence of the rubber content on the deformation behavior of nylon/rubber TPVs was investigated by IR-strain measurements on blends containing 40, 50, 60, and 70 wt % rubber. These measurements were performed at room temperature under dry conditions. The samples were stretched at a constant rate of 20%/min for 5 min, leading to a strain of 100%. After this the strain direction was reversed, while keeping the strain rate constant at 20%/min. In Figure 3 the phase morphology is given for the binary nylon6/EPDM-*g*-MA blends with an E/P ratio of 75/25 for the rubber phase, and in Figure 4 the phase morphology is shown for the binary nylon-6/EPDM-*g*-MA blends with an E/P ratio of 50/50 for the rubber phase. In these TEM micrographs the light area represents the rubber phase and the stained darker area the nylon phase.

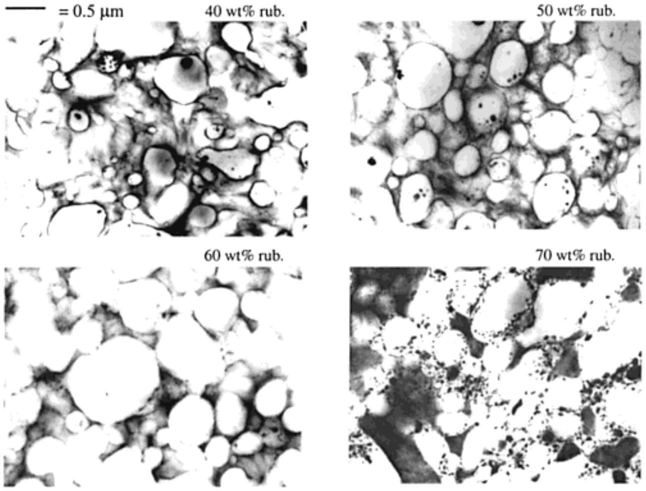

Figure 3. Phase morphology of nylon-6/EPDM-*g*-MA TPVs (40, 50, 60, and 70 wt % rubber) with an E/P ratio 75/25 for the rubber phase.

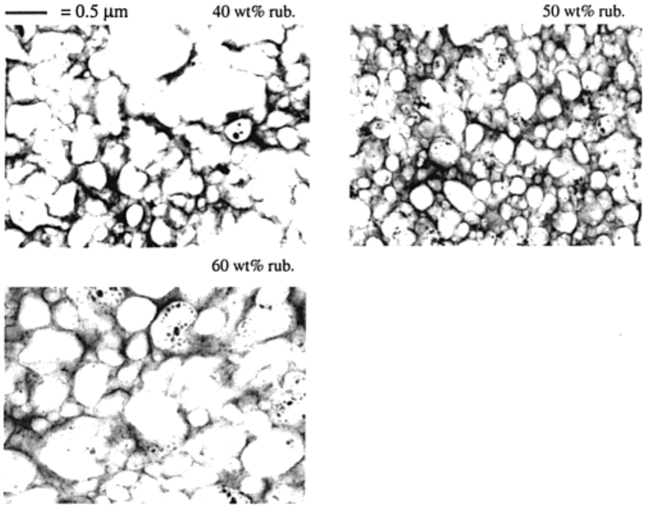

Figure 4. Phase morphology of nylon-6/EPDM-*g*-MA TPVs (40, 50, and 60 wt % rubber) with an E/P ratio 50/50 for the rubber phase.

The size of the rubber particles varies between 0.2 and 1 μm for the TPVs with an E/P ratio of 75/25 and between 0.2 and 0.6 μm for the TPVs with an E/P ratio of 50/50. The influence of the amount of rubber on the particle size is negligible for both systems.

The orientation of the EPDM phase is difficult to follow during IR-strain measurements for the EPDM rubber with an E/P ratio of 50/50. The IR-strain measurements on pure EPDM-*g*-MA show that only the peak at 720 cm^{-1} displays dichroism. For the nylon/rubber blends with an E/P ratio of 50/50 for the EPDM,

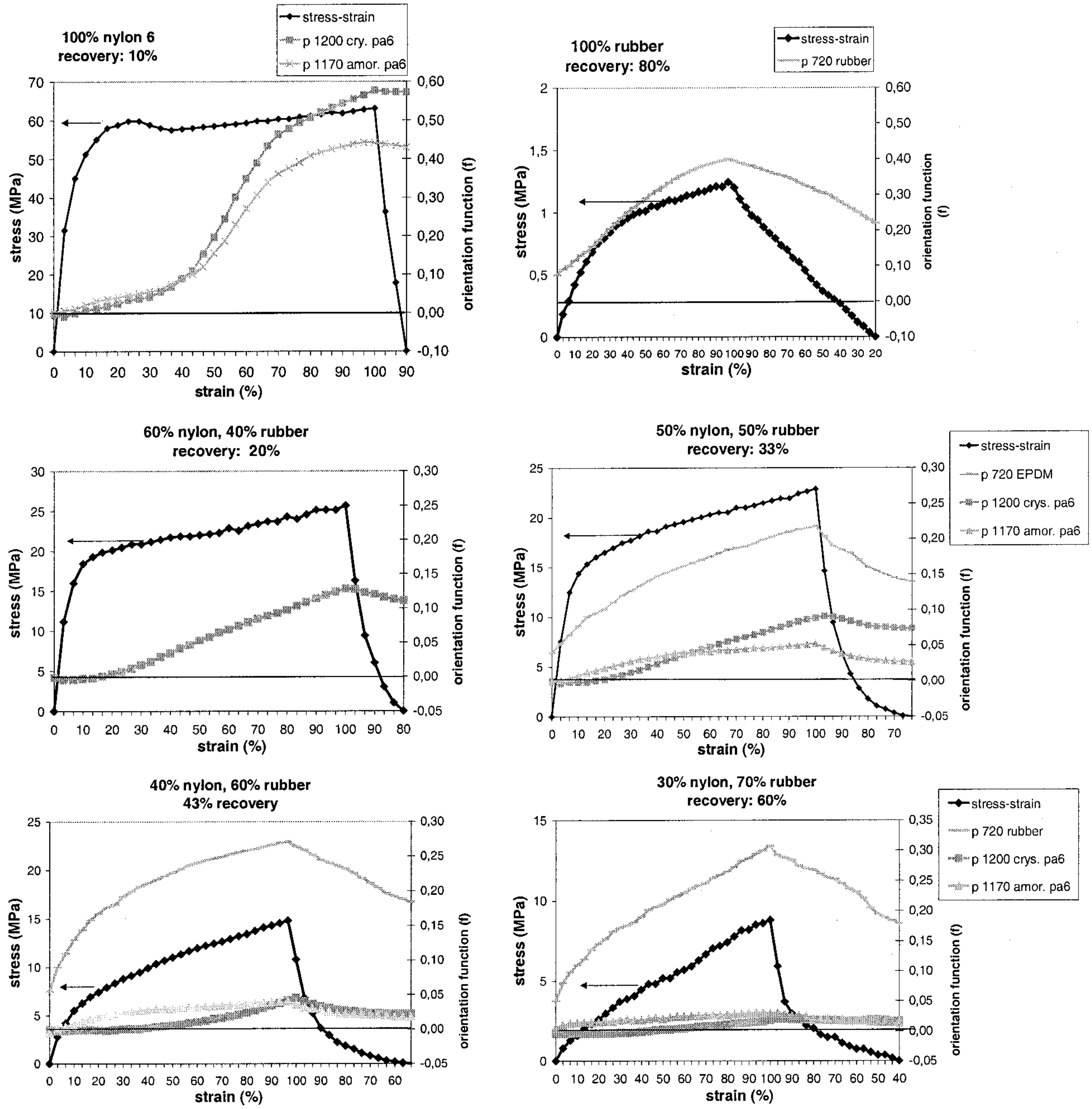

Figure 5. IR-strain recovery measurements for nylon/rubber TPVs with a crystalline rubber.

it is not possible to follow the orientation of the rubber phase. This is due to the fact that the 720 cm^{-1} peak is situated near a broad nylon peak, with a peak maximum at 685 cm^{-1}. And because of the low amount of crystalline ethylene sequences in this rubber, the absorption of light was not high enough to follow the rubber orientation. For the nylon/rubber blends with an E/P ratio of 75/25 for the EPDM phase the orientation of the rubber could easily be followed. The absorption of light is much higher for the characteristic crystalline ethylene sequences in the EPDM rubber with an E/P ratio of 75/25 compared to the more amorphous ethylene sequences for the EPDM rubber with an E/P ratio of 50/50. For that reason we call the EPDM rubber with an E/P ratio of 75/25 “crystalline” and with an E/P ratio of 50/50 “amorphous”, although the so-called amorphous rubber still shows crystallization behavior.[2]

The IR-strain measurements for the nylon/rubber TPVs with a crystalline rubber are presented in Figure 5. The left vertical axis shows the stress in the sample during stretching, while the right vertical axis shows the value of the different orientation functions. The measurements for the TPVs with an amorphous rubber are not presented due to the fact that the stress−strain and orientation behavior of the different phases are the same compared to the TPVs with a crystalline rubber.

Strain-recovery tests, which were used in combination with IR, showed that the amount of irreversible strain, i.e., the strain at which the stress reaches zero, is smaller when the sample contains more rubber. The blend with a rubber content of 70 wt % basically behaves like a rubber material and does not display a yield point. The blend morphology is also quite different compared to the other blend compositions; a more co-continuous morphology can be observed for this TPV with 70 wt % of rubber (see Figure 3). On the other hand, the nylon/rubber TPVs with 40, 50, and 60 wt % of rubber show a fine dispersion of the rubber in the nylon matrix. It can also be seen that the weight percentage of nylon in the samples influences the overall stiffness. The stress−

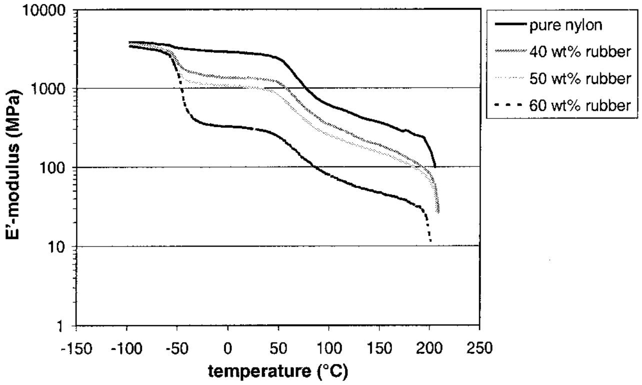

Figure 6. DMTA curves of nylon/rubber TPVs with different rubber concentrations at a frequency of 10 Hz.

strain curve of the sample with 60 wt % rubber clearly shows that it behaves differently from the samples with 40 and 50 wt % rubber; the 60 wt % rubber blend displays a more rubberlike behavior. This could lead to the conclusion that the nylon phase is no longer the matrix, although the TEM picture (Figure 3) reveals that the rubber is indeed dispersed in the nylon.

The different mechanical behavior of the 60 wt % rubber blend with a crystalline EPDM rubber is also seen in DMTA measurements for these blends with different rubber concentrations (see Figure 6). After the glass-transition temperature of the rubber, the storage modulus *E'* of the 60 wt % rubber blend drops more than would be expected for a simple composite material where the nylon phase forms the matrix, and the rubber is dispersed in very small particles. The reason for this behavior is that the interparticle distance between the rubber particles is so small (or the particles even touch each other) that the stress transfer across the morphology for the 60 wt % rubber blends is rather different than for the 40 and 50 wt % rubber blends. The material behaves mechanically more like a co-continuous system although the nylon still forms the matrix. Therefore, the shape of the yield point for this blend is rather different compared to the blends with 40 and 50 wt % rubber.

The orientation of both the crystalline and the amorphous phase of pure nylon increases rapidly beyond a certain strain percentage (see Figure 5); this is caused by necking of the nylon phase. The neck and thereby the orientation of nylon start to occur at the yield point, but the orientation is not visible for the infrared spectrometer until the neck really moves into the infrared beam. The orientation function in the neck after 100% strain is 0.6 for the crystalline phase and 0.45 for the amorphous phase. In the TPVs, however, the value of the maximum crystalline and amorphous orientation is much smaller compared to that of the pure nylon. Compared to the amount of crystalline orientation found in pure nylon after the yield point, only about 20% of the nylon would have reached the yield point after 100% strain for the 60 wt % rubber blends in order to get such a low average degree of orientation. For the 50 and 40 wt % rubber blends, the nylon phase will have reached the yield point by an amount of 30% and 50%, respectively. Although still half of the nylon phase reaches the yield point, the recovery remains very poor. The reason for this is that the elastic forces of the rubber phase are not sufficient to pull the plastically deformed nylon phase back into its original position. Obviously, the amount of rubber influences the degree of crystalline orientation during deformation (see also Figure 7). The weight percentage of rubber also influences the level of strain which has to be applied to the sample before the crystalline orientation starts. For the 40 wt % rubber TPV, the crystalline orientation starts after a strain of 20% is reached, and it increases with increasing amount of rubber. From the IR-strain plots it follows that the amorphous phase starts to orient earlier than the crystalline phase.

It also appears that almost all of the EPDM phase is stretched during deformation, especially for the 60 and 70 wt % rubber blends. The crystalline ethylene sequences in the EPDM phase start to orient right from the start of the tensile test; the orientation increases continuously and follows (for the 60 wt % rubber blend) the stress−strain curve. The orientation decreases when the strain rate is reversed, contrary to the nylon phase which is plastically deformed.

3.2. Influence of the Applied Strain on the Orientation and Recovery Behavior. The influence of the applied strain on the deformation behavior of nylon/rubber TPVs was investigated by IR-strain measurements on blends containing 50 and 60 wt % of the crystalline rubber (E/P ratio 75/25). The measurements were performed at room temperature under dry conditions. The samples were stretched to strains of 50%, 100%, and 200% at a constant rate of 40%/min. Figures 8 and 9 give a representation of the results.

It is shown that the recovery is improved when the rubber content is higher and when the applied strain on the sample is reduced. The recovery behavior as a function of the applied strain for the 50 and 60 wt % rubber TPVs decreases in the same manner with increasing applied strain (see Figure 10). The recovery behavior at 50% strain is excellent for both components, especially for the 60 wt % rubber TPV. If the applied strain is increased to 100%, the recovery of both blend

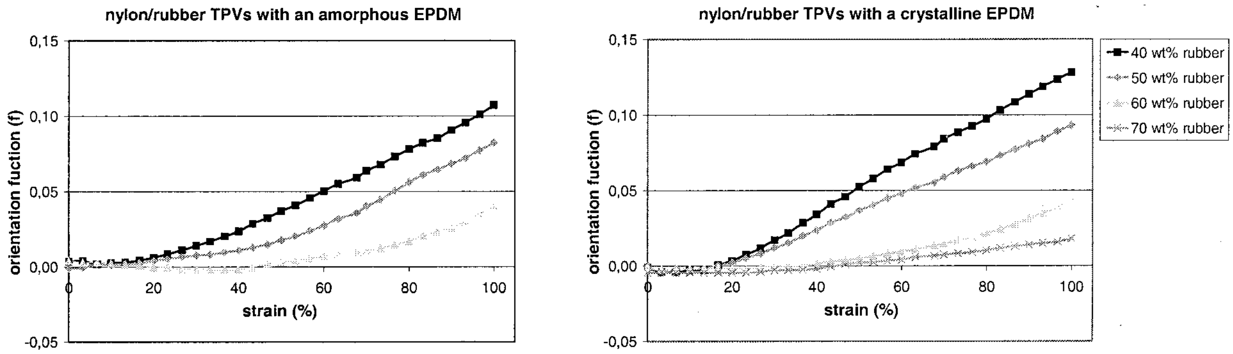

Figure 7. Crystalline orientation of the nylon phase for nylon/rubber TPVs.

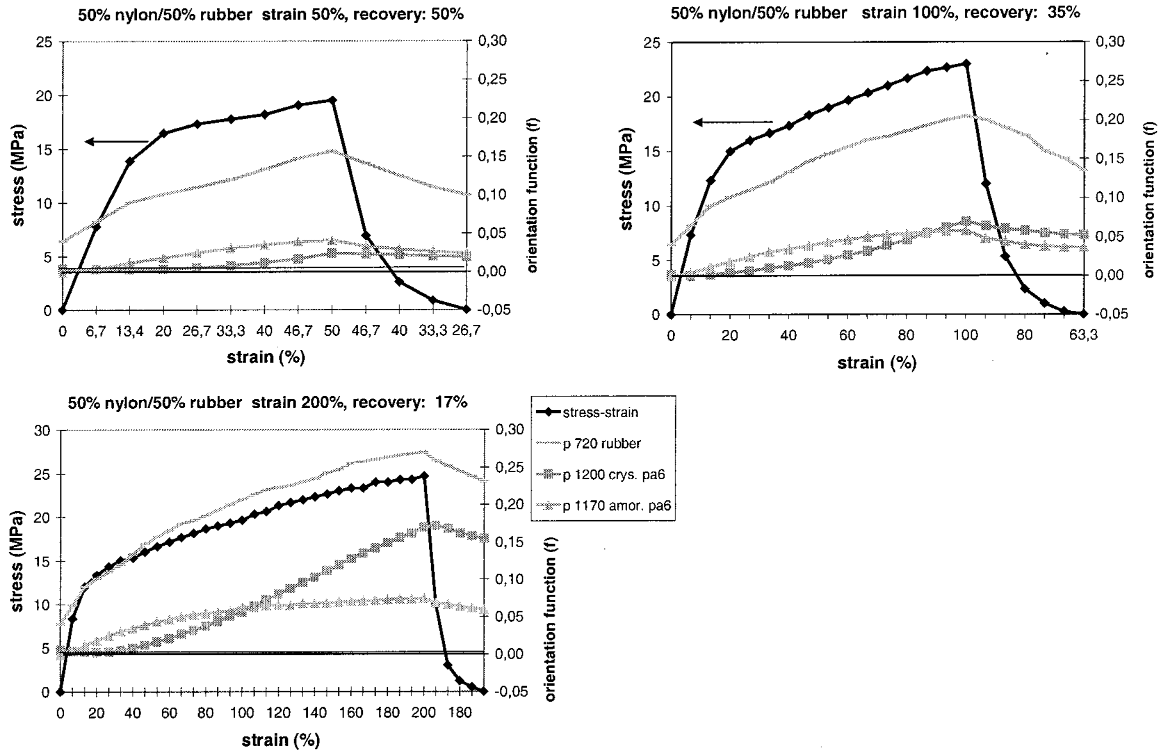

Figure 8. Influence of the applied strain on the orientation behavior for nylon/rubber TPVs with 50 wt % rubber.

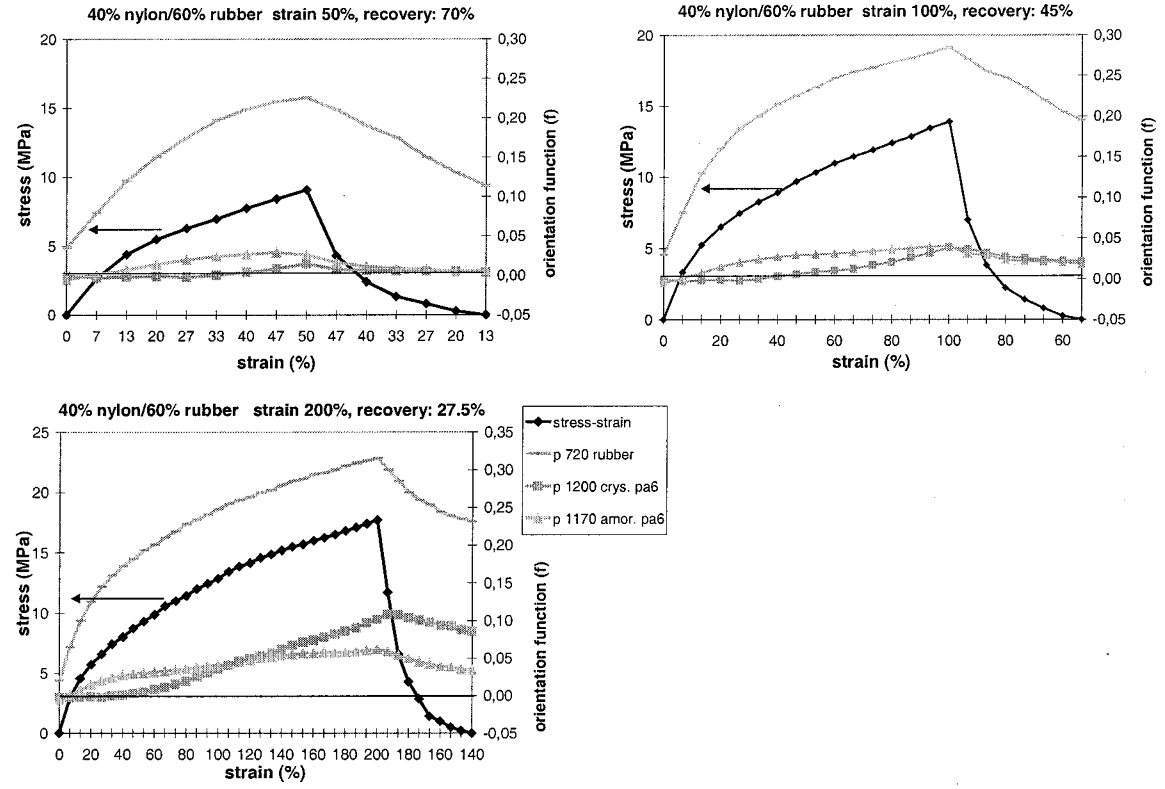

Figure 9. Influence of the applied strain on the orientation behavior for nylon/rubber TPVs with 60 wt % rubber.

compositions is considerably reduced; only the 60 wt % rubber blend still shows elastic behavior. Application of 200% strain also leads to a more significant loss in elastic behavior of the 60 wt % rubber TPV.

The crystalline orientation of the nylon phase as a function of the applied strain gives a good explanation for this behavior (Figure 10). At 50% applied strain the crystalline orientation is very low for both blend compositions. If the applied strain is increased to 100%, the crystalline orientation for the 60 wt % rubber blend remains very low compared to that obtained for the 50 wt % rubber blend. The crystalline nylon phase of the 60 wt % rubber blend becomes significantly oriented at an applied strain of 200%. From Figure 10 it can be seen that for both blend compositions there is a linear relation between the applied strain and the orientation

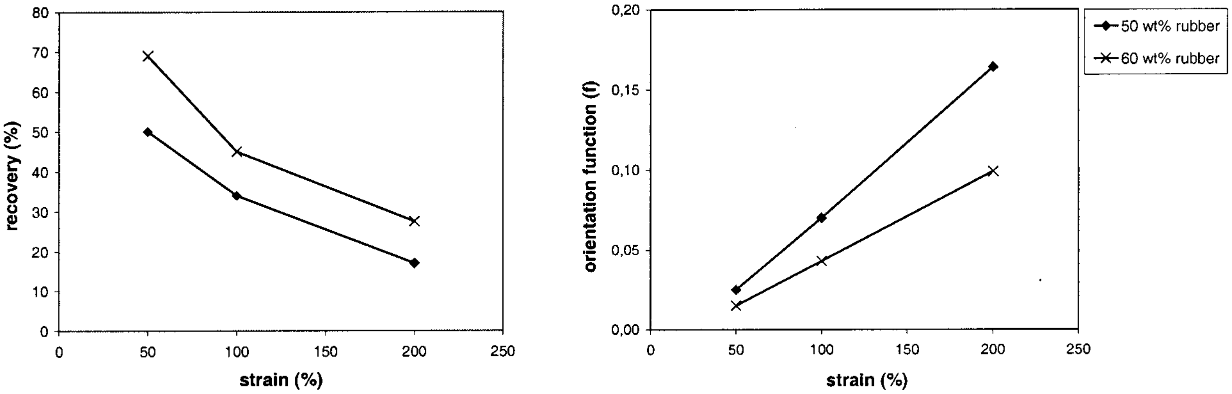

Figure 10. Recovery and crystalline orientation of the nylon phase as a function of the applied strain.

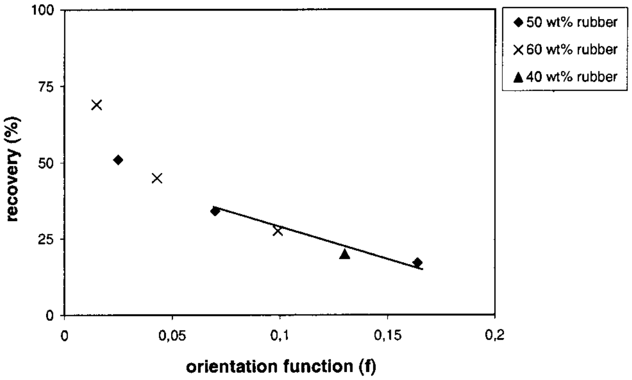

Figure 11. Recovery as a function of the orientation of the crystalline nylon phase for different nylon/rubber compositions.

of the crystalline phase; the increase of the orientation is steeper for the 50 wt % rubber blend.

As already mentioned in section 3.1, the amorphous phase of nylon starts to orient right from the beginning of the tensile test. This orientation immediately starts to follow a steep course and shows a more flat behavior after a strain of 50% is reached. On the contrary, the crystalline phase of nylon only begins to orient after a threshold strain is applied and displays a more significant orientation after 50% strain.

In Figure 11 the recovery is represented as a function of the orientation of the crystalline phase of nylon for both blend compositions. After a minimum amount of orientation has been reached, there appears to exist a linear relationship between the recovery and the orientation of the crystalline phase. This correlation is independent of the rubber concentration. After this threshold, the orientation of the crystalline phase inhibits a good recovery. The nylon phase becomes too much plastically deformed, and the elastic forces of the rubber are not strong enough anymore to pull the nylon back to its original state. This effect appears to be independent of the amount of rubber in the blend and the applied strain. It is important to remember that the crystalline orientation is dependent on the rubber content. Addition of the 40 wt % rubber (section 3.1) data point which is taken at 100% strain appears to fit perfectly with the linear correlation between the recovery and the crystalline orientation of the nylon phase.

The results from the IR-strain recovery measurements indicate that for a good recovery for a nylon/rubber TPV the nylon phase displays almost no plastic deformation. On the contrary, the rubber phase completely orients during deformation, especially for the blends with a very high amount of rubber (≥60 wt %). Similar results were also found by Soliman et al.[7] for PP/EPDM TPVs. They found that the complete EPDM phase is stretched during the tensile test, while only a small fraction of the PP matrix is deformed. These results were accounted for by a deformation model which assumes a very inhomogeneous deformation of the PP matrix and a good adhesion between the matrix and rubber phase. This model shows a high plastic deformation of the matrix which is only localized at the equatorial region of the rubber particles. This hypothetical model also explains fairly well the IR-strain recovery results of the investigated nylon/rubber TPVs. At low strains both the nylon matrix and the rubber phase deform elastically, and the applied deformation is almost completely recoverable. At higher applied strains (≥50%), the semicrystalline nylon matrix will be strained on average well beyond its yield strain and undergoes plastic deformation.

Plastic deformation will be initiated and concentrated at locations where the matrix ligaments are the thinnest. The ligaments localized transverse to the applied stress direction will bend or buckle, initially elastically and subsequently with increasing plasticity. Those ligaments which are laying in the stress direction will yield and draw. The thicker regions of the matrix will remain almost unyielded and act like rigid blocks at relatively lower strains. These rigid blocks will hold the rubber particles together, as suggested by Kikuchi et al.[3,4] and Kawabata et al.[5] The continuous substructure of the rubber particles and the only slightly deformed thicker regions of the matrix interconnect the rubber phase and give the ability to obtain a high degree of elasticity. Therefore, one can conclude that the thinner matrix ligaments will be highly plastically deformed but embedded in an elastic matrix.

If the elastic restoring force in the rubber phase is high enough, the highly stretched nylon parts could undergo reverse plastic deformation and obtain their original geometry. However, it is more likely that the elastic forces of the rubber phase will cause the highly plastically deformed nylon parts to bend or to buckle. This hypothetical model of inhomogeneous deformation and recovery behavior of TPVs is presented in Figure 12. On the basis of FEM analysis, Aoyama et al.[15] proved in the case of an ideal PBT/rubber TPV (50/50 wt %), in which the dispersed phase consists of perfect spheres, that the plastic deformation will be localized at the boundaries between these rubber spheres. The yielding of the matrix is thus induced at the equatorial region of the rubber particles, and even at a strain of

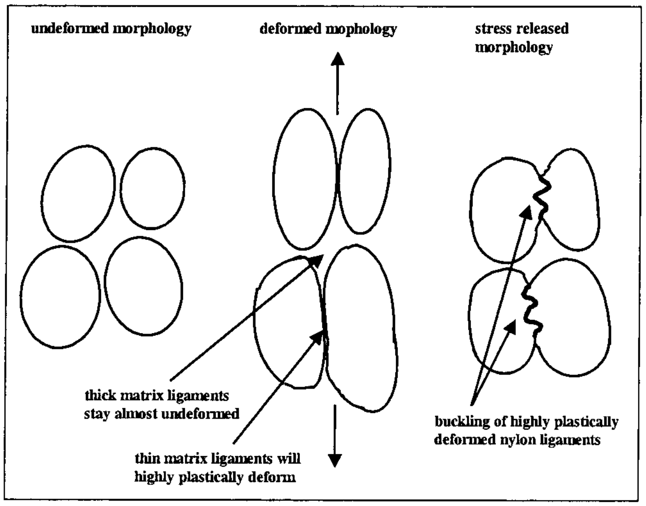

Figure 12. Inhomogeneous deformation model of a thermoplastic vulcanizate (TPV).

50%, the meridian region is locally preserved within the elastic limit at low stress.

3.3. Influence of the Temperature on the Orientation and Recovery Behavior. The influence of the temperature on the deformation behavior of nylon/rubber TPVs was investigated by IR-strain recovery measurements on blends containing 50 and 60 wt % of the amorphous rubber (E/P ratio 50/50). The recovery measurements were performed at 20 and 70 °C under dry conditions. The samples were stretched to 100% at a constant rate of 20%/min. Figure 13 gives a representation of the results.

The results of the IR strain-recovery experiments at a temperature of 70 °C show that the amount of irreversible strain, i.e., the strain at which the stress reaches zero, is smaller if the sample contains more rubber and if the recovery tests are performed at a temperature above the glass-transition temperature of nylon-6 (T_g(nylon-6) $\approx$ 60 °C). At this temperature the materials deform easier, and the yield point decreases markedly.

The amorphous phase of the nylon returns reasonably well to its initial form when the stress is released during measurements at a high temperature, as compared to the measurements at room temperature. The reason for this behavior at elevated temperatures is that relaxation of the amorphous phase takes place; as a consequence, the rubber phase is able to pull back the deformed nylon phase much easier. The recovery behavior of the well-known PP/EPDM TPVs is better compared to the nylon/EPDM TPVs for the reason that the glass-transition temperature of polypropylene is around 0 °C. From the results of the IR strain-recovery tests at a temperature above the glass-transition temperature of nylon-6, it follows that the recovery behavior of nylon/rubber TPVs can really be improved by lowering the glass-transition temperature of nylon-6. There are several plasticizers for nylon-6, in particular water and methanol.

4. Conclusions

The results from the IR-strain recovery measurements on nylon/rubber TPVs showed that for a good recovery the crystalline phase of the nylon matrix should almost not deform, and the amorphous phase should return reasonably well to its initial form when the stress is released. The rubber phase is almost completely stretched during deformation, espescially for the blends with a high amount of rubber (≥60 wt %). The stress−strain curves for the blends with a high amount of rubber shows the typical behavior of a

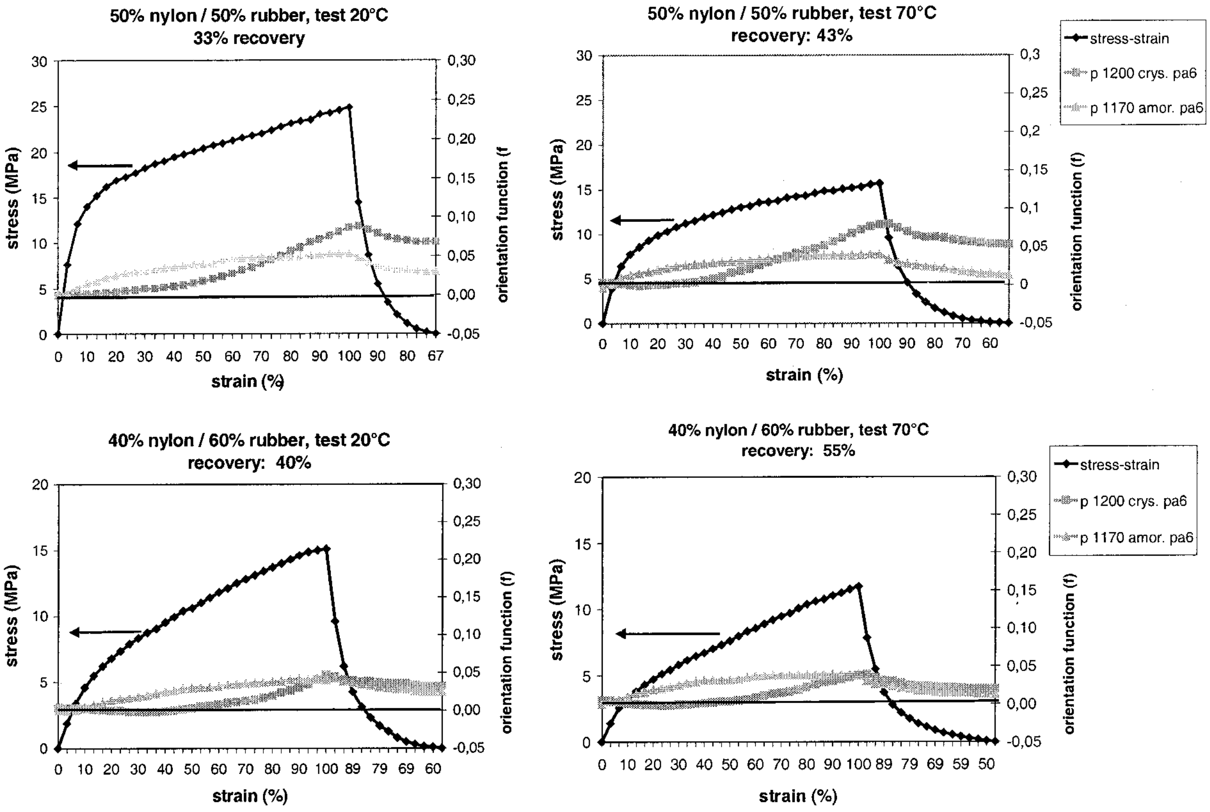

Figure 13. Influence of temperature on the orientation and recovery behavior of nylon/rubber TPVs with 50 and 60 wt % rubber.

thermoplastic elastomer with an E modulus which is lower than expected from a simple composite model and a broad “yield region”. These results can be accounted for by a model that assumes a very inhomogeneous deformation of the nylon matrix and a good adhesion between the nylon matrix and the dispersed rubber phase. At low strains both the matrix and the rubber phase deform elastically, and the applied deformation is almost completely recoverable. At high applied strains (≥50%), the semicrystalline nylon matrix will be deformed on average well beyond its yield strain and undergo plastic deformation. This plastic deformation will be initiated and concentrated where the matrix ligaments are thinnest. Further investigations should give more insight into the deformation mechanisms of TPVs. The study of the micromechanical deformation processes by real-time atomic force microscopy (AFM) will give more information about the orientation behavior of the rubber and matrix phase during deformation.

Acknowledgment. The authors are indebted to DSM Research, Geleen, The Netherlands, for the financial and experimental support of this project and to the Fund for Scientific Research Flanders (FWO-Vlaanderen) as well as to the Research Council KULeuven (GOA project).

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MA010651V