Self-healing properties of carbon nanotube filled natural rubber/bromobutyl rubber blends

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Abstract. In the present work, the development and characterization of an intrinsically self-healable material based on butyl imidazole modified bromobutyl rubber (BIIR)/natural rubber (NR) blends, which are filled with carbon nanotubes (CNTs) are reported. It was found that the addition of CNTs and the blending with NR significantly enhance the tensile strength of the BIIR composites. The use of butyl imidazole as physical cross-linker for the BIIR phase provides the blend composites the non-covalent bondings, which are responsible for their self-healing properties. Owing to the increase of the viscosity of the BIIR phase upon its physical crosslinking the island-matrix morphology of the blend changes over to a co-continuous structure. The preferential wetting of the CNT surface by the low-loading NR phase in the NR/BIIR blends can be explained by the good rubber-filler interaction between the linked phospholipids of the NR molecules and the π -electrons of the CNT surface. As a result, the favored localization of the CNTs in the NR phase strongly improves the electrical properties of the blends according to the double percolation theory. On the other hand it does not deteriorate the self-healing of the BIIR phase. The high electrical conductivity provides us a possibility to heat the blend by application of an electrical voltage in order to accelerate the self-healing process.

Keywords: rubber, self-healing, carbon nanotubes, selective filler wetting

1. Introduction

Self-healing polymers and especially elastomers have gained more and more attention in material science because of their interesting scientific aspects and variety of applications [1–8]. Such materials can be used as sealing joints, impact protection, insulation and shock-absorbing layers, anticorrosion coatings for metals, as well as adhesives or paints [9, 10]. They are, however, susceptible to damage induced by mechanical, chemical, thermal, UV radiation, or a combination of these factors. This could lead to the formation of micro-cracks or grooves deep within the structure, where detection and external intervention

by conventional methods are difficult or impossible [11]. In this context, the concept of self-healing polymeric materials proposed by Jud *et al.* [5] in 1980s and later inspired by Dry and Sottos [6] and White *et al.* [7] has been expected to fill this technological gap. The successful development of self-healing polymeric materials offers great opportunities for broadening the applications of these lightweight materials for the manufacture of structural and critical components [9, 12–16].

Recently, our group developed a self-healing rubber compound by a simple ionic modification of commercially available bromobutyl rubber (BIIR) [17].

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For this, BIIR was converted with 1-butylimidazole as described first by Parent *et al.* [18]. The imidazolium ions originated by this reaction formed a non-covalent network by ionic association. Owing to the reversibility of the network formation, the material exhibited pronounced self-healing behavior. The BIIR used here is known for its low gas permeability, good thermal and oxidative stability, as well as excellent moisture barrier, chemical resistance properties and vibration damping [19]. These characteristics can make it suitable for the inner lining of tires. However, the absence of a covalent network structure and the formation of relatively weak bonds originated by ionic clusters within BIIR generally lead to lower mechanical properties, in particular, low stiffness, poor tensile properties, and creep resistance behavior. Furthermore, a slow self-healing rate and a required high trigger temperature limit the application of this interesting material. Thus, the developed ionically modified BIIR seems to be not suitable for practical application unless the mechanical properties will be enhanced. In this context, in the past, different works [20–27] have been done as for example mixing rubbers with ionomer in order to modify their mechanical properties and self-healing behavior, especially NR/BIIR blends. For instance, Lemieux and Killgoar [21] reported the increase of damping and thermal stability with increasing BIIR loading. On the other hand, Rodgers *et al.* [23] found an increase in gas barrier property with BIIR content from 60 to 100 wt%, whereas tensile strength and rebound resilience of the blends decreased. In addition, Lewis *et al.* [24] predicted the effects of the blend ratios on the cure characteristics and physical properties of NR/BIIR blends using a statistical experimental design. The predicted results showed that the properties of the blends are dominated by the NR content. Furthermore, an incorporation of conventional fillers or fibers enhanced the strength of the rubber compounds [28] and blends [29, 30], but, at the same time deteriorated the self-healing process significantly [31, 32]. As an alternative, nanofillers like carbon nanotubes (CNTs) in a low amount may enhance the mechanical properties of self-healing rubbers because of their high aspect ratio and large surface area available for stress transfer as well as their exceptionally high Young's modulus and excellent electrical and thermal properties. Not only the mechanical reinforcement but also the electrical conducting nature of the composites may be exploited by application of an electric

potential to generate heat within the rubber matrix, which could offer an acceleration of self-healing. In the present work, the dispersion of CNTs into ionically modified NR/BIIR blends will be investigated by variation of the material and mixing parameters. The influence of the interactions between the imidazolium groups, the CNTs, and the rubber matrix as well as the dispersion and phase selective localization of CNTs on the self-healing process of the rubber blends are the target of the present work.

2. Experimental

2.1. Materials and blend preparation

Bromobutyl rubber (BIIR) LANXESS X_Butyl™ BB X2 (Lanxess) with a halogene content of 1.95 wt% was used. The Mooney viscosity ML 1+8 (125 °C) is 46 MU. Natural rubber (NR) Standard Malaysian Rubber (SMR10) (Weber & Schaefer GmbH) was used as blend partner for BIIR. NR was masticated by means of a two-roll mill before use in order to obtain a Mooney viscosity value of about 45 MU, which is similar to that of the other blend partner. Multi-walled carbon nanotubes (CNTs) Nanocyl™ NC7000 (Nanocyl S.A., Belgium) were used as filler. The 1-butyl imidazole (Im) used in our study was received from Sigma-Aldrich, Steinheim, Germany. The CNT/Im/NR/BIIR 5/4/30/70 composites were prepared in an internal mixer (Rheocord 300p, ThermoHaake) by keeping the following mixing conditions: initial chamber temperature T_A of 35 and 80 °C, respectively, rotor speed of 60 rpm and fill factor of 0.78. The composition of the blends and the mixing temperature T_A are given in Table 1. After mixing, conventional sulfur curing was omitted. The mixtures were compression-molded at 120 °C under 100 bar for 20 min to obtain a sheet with a thickness of 2 mm used for morphological and mechanical testing as well as self-healing characterization.

2.2. Experimental

Optical microscopy

Optical microscopy was used to characterize the CNT macrodispersion. The ratio of the surface of non-dispersed agglomerates to that of the image, A/A_0 , is a

Table 1. Recipe and mixing temperature T_A

Sample	NR	BIIR	CNTs	Im	Mixing temperature (T_A)
S7	30	70	5	0	35 °C
S15	30	70	5	4	35 °C
S17	30	70	5	4	80 °C

measure for the filler macrodispersion. The lower the value A/A_0 the better the dispersion of the filler.

Tensile test of the virgin and self-healed samples

Stress-strain measurements were performed at room temperature with a cross-head speed of 200 mm/min according to ISO 37 using a tensile tester Z005 (Zwick/Roell). Rectangular test specimens ($2 \times 5 \times 50 \text{ mm}^3$) were used. All data presented are the average of five independent measurements. For the characterization of the self-healing process the samples were cut at the middle of its length by a razor blade. The cut surface was brought together and the samples were then stored in an oven at 120°C for 10 min. After removing from the oven they are allowed to self-heal for 24 h before performing the tensile test.

Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) measurements were performed on a TEM LIBRA 120 MC (Carl Zeiss SMT, Oberkochen, Germany) with an acceleration voltage of 120 kV using the zero loss mode. For this, ultrathin sections with approximately 60 nm thickness were cut with a diamond knife (35° cut angle, DIATOME, Switzerland) on a cryo-ultramicrotome EM UC6/FC6 (Leica, Austria) at -160°C . The sections were collected on carbon coated copper grids.

Measurement of the sample temperature development by applying an electrical voltage

Rectangular samples with two ends coated by silver were fixed by two clamps. The clamps were connected with a voltage source, and an average voltage of 15 V was applied. The sample temperature increased as a result of the Joule effect. The temperature of the sample was measured using a thermocouple.

Current initiated local healing

In the middle of a 2 mm thick compression molded sheet of the blends, a 5 mm slit was introduced with

Figure 1. Sample preparation for the current initiated local healing procedure

a razor blade (see Figure 1). In order to improve the contact with electrodes, the sheet was coated with a silver paste at the ends of the slit. Then, two electrodes were placed near the slit and a voltage of 15 V was applied for 10 min. After that, a dumbbell test specimen with the healed slit was punched out and tested by stress-strain measurements.

Measurement of the electrical conductivity

Measurement of the electrical conductivity of virgin samples was carried out at room temperature by means of a multimeter 2750 (Keithley). The shape of the conductive test specimens was a rectangular strip, the ends of which were coated by silver paste in order to receive a good contact with the electrodes.

The electrical conductivity was measured for the seal-healed samples during the seal-healing process.

Contact angle measurement

Sessile drop contact angle measurements were conducted with the automatic contact angle meter OCA 40 Micro, DataPhysics for the determination of the surface tension of the rubbers.

Extraction experiment for the determination of the bound rubber content

For the investigation of the rubber-filler gel of the blends, 0.1 g of each raw mixture was stored in 100 mL chloroform at room temperature. Upon seven days the rubber-filler gel was taken out and dried up to a constant mass. The rubber content in the gel $L^{B(NR/BIIR)}$ as a measure for the wetting behaviour of CNT surface by the NR and BIIR component was determined according to Equation (1) [33]:

$$L^{B(NR/BIIR)} = \frac{m_2 - m_1 \cdot c_{CNT}}{m_2} \quad (1)$$

The mass m_1 corresponds to the rubber compound before extracting. m_2 is the mass of the rubber-filler gel, which is the sum of the undissolvable rubber part and the mass of CNTs. c_{CNT} is the mass fraction of CNTs in the single rubber mixture or binary blends. For a NR/BIIR blend the rubber layer $L^{B(NR/BIIR)}$ is the rubber part in the rubber-filler gel and consists of two contributions according to Equation (2):

$$L^{B(NR/BIIR)}(t) = L^{B(NR)}(t) + L^{B(BIIR)}(t) \quad (2)$$

$L^{B(NR)}$ and $L^{B(BIIR)}$ can be determined by means of a calibration curve. For creation of the calibration curve, blends with different NR/BIIR ratios were prepared and investigated by FTIR according to the procedure described in our previous work [33]. FTIR spectra were recorded by the use of a FTIR spectrometer equipped with a germanium single ATR cell. The peaks at 1376 cm^{-1} (CH bending vibration in NR) and 1366 cm^{-1} (CH_3 flexural vibration in BIIR) were taken for calculation of the ratio of the surface under peak A^{NR}/A^{BIIR} . The correlation between the A^{NR}/A^{BIIR} ratio and the given NR/BIIR mass ratio can be established, and based on this correlation the ratio $L^{B(NR)}/L^{B(BIIR)}$ of the rubber-filler gel can be determined experimentally.

The selective wetting of CNTs in the NR/BIIR blend can be calculated according to the Equations (3) and (4):

$$\frac{S^{B(NR)}(t)}{S^{B(BIIR)}(t)} = \frac{L_P^{BIIR}}{L_P^{NR}} \cdot \frac{L^{B(NR)}(t)}{L^{B(BIIR)}(t)} \quad (3)$$

$$S^B = S^{B(NR)}(t) + S^{B(BIIR)}(t) \quad (4)$$

$S^{B(NR)}$ and $S^{B(BIIR)}$ are the CNT surface fractions wetted by the NR and the BIIR phase of the blend, respectively. t is the mixing time. S^B is the total filler surface wetted in the blend. L_P^{NR} and L_P^{BIIR} are the saturated rubber contents in the gel of the single compounds. They can be determined by extraction experiments of the samples after a mixing time of 20 min.

3. Results and discussion

3.1. Online conductance and CNT dispersion in 30/70 NR/BIIR blends

The online conductance curves recorded during the mixing process of CNT/NR/BIIR blends without and with imidazole at 35 and 80 °C, respectively, are shown in Figure 2. The blend mixed at 35 °C in presence of imidazole shows the highest online conductance that certainly is related to the better CNT dispersion. The low online conductance values of the imidazole containing sample mixed at 80 °C and the sample without imidazole are explained by the poor filler dispersion. The morphology of the three blends taken out at the end of the mixing process was studied by optical microscopy. The macrodispersion A/A_0 of each sample is given at the images. In the image of the blend without imidazole a number of undispersed CNT agglomerates with an average diameter of 40 μm is observed. A macrodispersion A/A_0 of 15% was determined. This poor dispersion causes a low electrical conductivity of the blend of $2.5 \cdot 10^{-15}\text{ S/cm}$. By addition of imidazole at 80 °C the number of large CNT agglomerates is reduced with a macrodispersion A/A_0 of 8% and an electrical conductivity of $4.6 \cdot 10^{-11}\text{ S/cm}$. By mixing at 35 °C the macrodispersion reduces to 3%. This corresponds well with the high value of the online conductance of $4.6 \cdot 10^{-3}\text{ S/cm}$. The choice of T_A of 80 °C aimed to initiate the reaction between the BIIR phase and the imidazole forming an ionically modified butyl rubber. It was expected that the formed imidazolium cation will interact with the π electrons of the CNT

Figure 2. Online conductance curves and CNT dispersion as well as electrical conductivity of different NR/BIIR blends

surface and thus that enhances the rubber-filler interaction leading to a better dispersion of the CNTs in the rubbers. However, according to the results shown in Figure 2 the improvement of the CNT dispersion was insignificant after mixing at 80 °C. The reason was found to be related to the morphology of the blends which will be discussed in the next chapter.

3.2. CNT selective wetting in 30/70 NR/BIIR blends

Beside the amount, the structure and the dispersion of the filler the selective wetting of the filler by the blend components is the most important factor influencing the mechanical and electrical properties of a filled rubber blend. On the basis of the *Z-model* proposed in our previous work [34], the selective wetting of the CNT surface at the thermodynamic equilibrium state can be predicted according to Equations (5) and (6):

$$\frac{S_{eq}^{B(NR)}}{S_{eq}^{B(BIIR)}} = n_{NR/BIIR} \left(\frac{\gamma_{BIIR-F}}{\gamma_{NR-F}} \right)^2 = n_{NR/BIIR} \left(\frac{\gamma_{BIIR} + \gamma_F - 2\sqrt{\gamma_{BIIR} \cdot \gamma_F}}{\gamma_{NR} + \gamma_F - 2\sqrt{\gamma_{NR} \cdot \gamma_F}} \right)^2 \quad (5)$$

$$S_{eq}^{B(NR)} + S_{eq}^{B(BIIR)} = 1 \quad (6)$$

$S_{eq}^{B(NR)}$ and $S_{eq}^{B(BIIR)}$ are the filler surface fractions wetted by the NR and BIIR phase of NR/BIIR blends at the equilibrium state. $n_{NR/BIIR}$ is the mass ratio of NR to BIIR in the blend. γ_{BIIR-F} and γ_{NR-F} are the interfacial tensions between the polymer and the filler. γ_{NR} , γ_{BIIR} and γ_F are the surface tension values of the polymer components and the filler, respectively. In the present work $\gamma_{NR} = 22$ mN/m, $\gamma_{BIIR} = 25$ mN/m, and $\gamma_F = 30.5$ mN/m were experimentally determined. The surface tension of NR was corrected further by

taking into consideration the effect of the phospholipid linked to α -terminal of the NR molecules using the *Z-model*. The corrected value $corr \gamma_{NR} = 26$ mN/m was determined in our previous work [35]. Setting the surface tension values γ_{BIIR} and $corr \gamma_{NR}$ of the rubber components of BIIR and NR into the *Z-model* with $n_{NR/BIIR} = 0.428$ for the 30/70 NR/BIIR blend, a Z-shaped master curve can be created demonstrating the filler surface fraction wetted by the BIIR phase $S_{eq}^{B(BIIR)}$ in dependence on the filler surface tension as seen in Figure 3a. Fitting the CNT surface tension $\gamma_F = 30.5$ mN/m into the master curve a CNT surface fraction wetted by the BIIR phase $S_{eq}^{B(BIIR)}$ of 0.32 was found at the thermodynamic equilibrium state.

The experimental determination of the CNT selective wetting in the NR/BIIR blend was carried out using the *wetting concept* [33, 34]. Figure 3b presents two FTIR spectra of a gel of a NR/BIIR blend received by extraction. Two spectra of the same gel were recorded using a germanium and a diamond ATR crystal, respectively. Because of the strong IR adsorption of CNTs in the gel the signal of the bound rubber becomes very weak. As seen in Figure 3b the diamond ATR crystal is not able to distinguish the peaks of both rubber components. Using a germanium ATR crystal, two characteristic peaks of the bound rubber of the NR and BIIR phase were clearly identified. The ratio of the area under the peaks A^{BIIR}/A^{NR} can be determined from the spectrum. Using the calibration curve, the ratio $L^{B(BIIR)}/L^{B(NR)}$ is also calculated according to our previous work [33]. Setting the value of $L^{B(BIIR)}/L^{B(NR)}$ and $L_p^{BIIR} = 0.5$ and $L_p^{NR} = 0.7$ for the mixing time t of 20 min into Equations (3) and (4), a CNT surface fraction $S^{B(BIIR)}$ of 0.2 wetted by the BIIR phase and $S^{B(NR)}$ of 0.8 wetted by NR phase were determined. This experimental result corresponds very well with the prediction made by the *Z-model*. The preferential

Figure 3. Prediction of the selective wetting of CNTs in the blend using the *Z-model* (a) and FTIR spectral of the gel of the blend (b)

wetting of CNTs by the NR phase can be explained by the presence of the phospholipid linked to the end of the NR chains. These structures can undergo specific interactions with the CNTs, i.e. the ammonium cation N^+ of the phospholipids can interact with the CNT surface *via* cation– π interaction forming stable linkages beside the Van der Waals bondings. The cation– π interaction was proposed by Ma and Dougerly [36] and Fukushima and coworkers [37, 38] as main linkage between CNTs and an ionic liquid. Based on this experimental result it can be postulated that NR and BIIR wet CNTs simultaneously in the earlier mixing period. The linked phospholipids can act as anchor points firmly bonding NR terminal with the CNT surface. With increasing mixing time NR can enhance its interactions with CNTs through Van der Waal bondings between its backbone and the CNT surface. Through conformational rearrangements and thermodynamic driving forces, NR molecules gradually replace BIIR molecules on the CNT surface.

The TEM image of the blend CNT/NR/BIIR 5/30/70 without imidazole is shown in Figure 4a. Most of the CNT individuals are found in the NR domains (dark area) that is in accordance with the prediction and experimental results shown in Figure 3. The localization of the CNTs in the NR domains is one of the reasons for the very low value of the electrical conductivity of this blend (Figure 2), because no percolation network was formed in the blend. That is also the reason for the ineffectiveness of the mixing process at 80 °C. As discussed above, the mixing at high temperature aims to increase the interaction between BIIR and CNTs. However, very less CNTs are localized in the BIIR phase.

The island-matrix morphology with the NR domains distributed in the BIIR matrix (bright area) was also found for the NR/BIIR blend with low loading NR by Rattanasom *et al.* [30]. They reported that the

blend morphology became co-continuous when the NR loading increased to 50%. Achalla *et al.* [39] examined the phase morphology of the unfilled NR/BIIR blends using Atomic Force Microscopy (AFM), they found that NR is the dispersed phase when BIIR content is larger than 50 wt%. In addition, a co-continuous morphology was observed for a 50/50 NR/BIIR blend. By addition of imidazole, the TEM investigation of the blends presented in Figure 4b and 4c makes clear that the CNT filled NR domains connect with each other forming a co-continuous structure. The continuous CNT/NR phase forms conductive pathways which lead to the high conductivity of this blend. The change in the blend morphology from an island-matrix structure to a co-continuous structure is related to the change of the BIIR/NR viscosity ratio. According to [40, 41] the morphology of a binary polymer blend can be predicted by taking into consideration the factor ψ , which is calculated by the viscosity ratio and the volume ratio given in Equation (7). If ψ approaches unity, a co-continuous phase is expected (Figure 5). If it is larger than 1, an island-matrix morphology with a NR matrix is predicted. If it is smaller than 1, a morphology with NR domains distributed in the BIIR matrix will be formed. Setting the experimentally determined Mooney viscosities η_{BIIR} of 46 MU and η_{NR} of 45 MU as well as the volume fraction ϕ_{BIIR} of 0.7 and ϕ_{NR} of 0.3 into Equation (7) a value of ψ of 0.43 was determined which indicates an island-matrix structure with NR domains in the BIIR matrix as evidenced by the TEM image (Figure 4a). By addition of imidazole the viscosity of BIIR increases significantly because of the formation of an ionic network as illustrated in Figure 5. The Mooney viscosity of BIIR increased to 75 MU upon addition of imidazole, which shifts the value of ψ to 0.72. This value may indicate a formation of a co-continuous morphology as seen in Figure 4b and 4c.

Figure 4. TEM image of CNT/NR/BIIR blend without imidazole (a), change of the blend morphology caused by addition of imidazole presented at different magnifications (b, c)

Figure 5. Torque-time curves of BIIR mixed with imidazole measured in a moving die rheometer at different temperatures (a), structure of the imidazolium ions formed at high temperature (b), schematic presentation of the formation of ionic cluster as physical cross-links (c)

$$\psi = \frac{\frac{\eta_{\text{BIIR}}}{\eta_{\text{NR}}}}{\frac{\phi_{\text{BIIR}}}{\phi_{\text{NR}}}} \quad (7)$$

The effect of vulcanization on the viscosity of the NR/BIIR and NR/CIIR blends and the blend morphology was also investigated by Turturro *et al.* [42]. It was found that the change of the viscosity of the blend components lead to a change of the blend morphology during the vulcanization.

3.3. Thermally activated self-healing of CNT/NR/BIIR blends

The grafting reaction of the NR/BIIR blend with butyl imidazole was followed in a moving die rheometer. Prior to this, premixing was performed at 35 °C in an internal mixer (sample S7 and S15). The torque-time curves of the blends measured at different temperatures are presented in Figure 6a. For the blend without imidazole, the torque remains unchanged with time. For the blends with imidazole

the torque increases with time and temperature. This is related to the formation of ionic imidazolium groups (Figure 6b) which are able to form an ionic network (Figure 6c). The ionic network formation and the self-healing behavior of the unfilled BIIR have already been discussed in details in our previous work [17]. The ionic clusters restrict the molecular mobility of the polymer matrix and as a consequence, the viscosity and the torque increase with progressing reaction. At 150 °C, the cross-linking is reversible and the torque-time curve shifts to a lower level as discussed in [34, 43–45].

The stress-strain curves of the healed NR/BIIR blends with different blend ratios are shown in Figure 7. It is clear that the stress $\sigma_{200\%}$ determined at the strain of 200% increases strongly with increasing NR content which is in line with the results of the virgin samples. The improvement of the strength of NR/BIIR with increasing NR loading blends was also found in different works reported in the past [24]. The elongation of the virgin samples is insignificantly different upon addition of NR and it lies

Figure 6. Morphology of NR/BIIR blend in dependence on the viscosity ratio and volume ratio

Figure 7. Effect of the NR loading on the thermally activated self-healing behavior of CNT filled NR/BIIR blends with imidazole

in the range of about 900% to 1000%. However, the elongation of the healed samples reduces markedly as seen in Figure 7 since the samples become harder and the unhealable rubber portion increases. That indicates the worsening of the self-healing behavior of the NR/BIIR blends with increasing NR content.

3.4. Joule heating triggered self-healing of CNT/NR/BIIR blends

Because of slow self-healing of CNT/NR/BIIR blends taking place at room temperature, an acceleration of the process at elevated temperatures by thermal heating [17] electrically resistive heating [46], or application of visible light [47] seems to be reasonable. In the present work, thanks to the high conductivity of the CNT/NR/BIIR blends with imidazole, the self-healing behavior of these blends can be accelerated by applying an electrical voltage. In order to demonstrate the possibility of healing CNT/NR/BIIR blend by Joule heating, a special healing procedure was designed (see Figure 8). For the testing, the sample was not punched out from the plate. Instead, a deep slit was introduced in the middle of the plate between two areas of silver coating according to Figure 1.

Then, the plate was punctually heated near the slit by applying a voltage of 15 V. The sample temperature was measured using a contact thermocouple. The sample temperature at the cut position increases up to 100 °C (Figure 8d and 8e). An infrared camera was used to obtain the surface temperature distribution of the heated zone. This setup enables us to heal the sample effectively. As demonstrated by the optical micrograph the cut (Figure 8a) was mended after applying the voltage as seen in Figure 8f.

Figure 9a shows the stress-strain curves of CNT/Im/NR/BIIR blends as received after compression molding (virgin) and after the Joule heating mending procedure. The virgin sample exhibits an elongation at break of 980%, while the sample healed by Joule heating exhibits an elongation at break of only about 400%.

Optical microscopic images of the virgin blend (Figure 8a) and of the healed blends (Figure 8f and 9b) are shown. Accordingly, the interface between the two sections of the sample is mended. An unhealed gap is also visible, which is attributed to an insufficient contact between the two sample parts.

Figure 8. Self-healing of CNT/NR/BIIR blend accelerated by Joule heating

Figure 9. Stress-strain curves of CNT/NR/BIIR blend (a) and microscopic image of the interface mended by Joule heating (b)

During the self-healing process, recovery of the mechanical properties as well as other physical properties takes place. Recovery of the electrical conductivity of a physically damaged sample by self-healing is a very interesting aspect, which might be highly beneficial for applications in energy storage and microelectronics. Damaged electronic devices might be able to repair themselves on site, instead of requiring replacement. In order to characterize the recovery of the CNT network during the self-healing process, a rectangular sample was considered. The two opposite sides of the sample were coated with silver paste to get a good contact with the electrodes. This sample was then cut in the middle into two parts, which then immediately are brought into contact for mending. During the healing process at room temperature and higher temperatures, the electrical resistance was measured. The results are shown in Figure 10. The resistance at room temperature does not change significantly, because the chain inter-diffusion process is not accelerated, which is important for the reformation of the CNT network and thus for the recovery of the conductivity. In contrast, the resistance decreases strongly, when the temperature increases. That indicates a re-formation of the CNT network in the interphase during the healing process.

3.5. Anisotropic morphology of CNT/NR/BIIR blends

As shown in Figure 4, the filled NR/BIIR blend without imidazole shows a morphology comprising isolated CNT filled NR domains distributed in the BIIR matrix. In order to investigate the effect of the flow direction on the formation of blend morphology we modified the compression mould as shown in Figure 11a. Under pressure during compression moulding the mixture flows into the channel (Figure 11b). The morphological characterization was conducted by TEM in flow and perpendicular direction. The micrographs are shown in Figure 11c and 11d. It is clear that during flowing into the channel the filled NR domains were elongated resulting in an anisotropic morphology, and as a result, an anisotropy in mechanical and electrical properties of the blend is expected. This morphology is found to be stable with temperature that may be related to the rigid CNT network inside the elongated NR domains. In literature a number of authors [48, 49] tried to originate CNT orientation in rubber compounds, for example, by the use of a two-roll mill and sheeted off at the smallest nip gap. However, the orientation of CNTs was hardly observed and it disappeared during the vulcanization process at high temperature as a result of the re-

Figure 10. CNT network reformation during the self-healing process

Figure 11. Anisotropic morphology of CNT/NR/BIIR blend without imidazole

Figure 12. Isotropic morphology of CNT/Im/NR/BIIR blend with imidazole

laxation of the rubber molecules. The extraordinary and stable CNT orientation observed in the present work may open a new route to create anisotropy rubber composites.

By adding imidazole, the blend presents a co-continuous morphology as discussed above. The co-continuous morphology is not influenced by the flow inside the channel as shown in Figure 12.

4. Conclusions

In the present work, the mechanical properties and especially the self-healing behaviour as well as the electrical conductivity of carbon nanotube filled NR/BIIR blends were characterized. The addition of CNTs and the blending with NR significantly en-

hance the tensile strength of the imidazole/BIIR composites. The use of butyl imidazole as physical cross-linker for the BIIR phase provides the blend composites the non-covalent bondings, which are responsible for their self-healing properties. The preferential wetting of the CNT surface by the low-loading NR phase in the NR/BIIR blends can be explained by the good rubber-filler interaction between the linked phospholipids of the NR molecules and the π -electron of the CNT surface. As a result, the favored localization of the CNTs in the NR phase strongly improves the electrical properties of the blends according to the double percolation theory on the one hand, and on the other hand it does not deteriorate the self-healing of the BIIR phase. Our work

also demonstrates that the self-healing process can be locally triggered by Joule heating for the composites with high electrical conductivity.

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