Effect of the Cross-Linking Process on the Electrical Resistivity and Shape-Memory Behavior of Cross-Linked Carbon Black Filled Ethylene-Octene Copolymer

Hai Hong Le, Zulfiqar Ali, Mathias Uthardt, Sybill Ilisch, Hans-Joachim Radusch

Center of Engineering Sciences, Martin Luther University Halle-Wittenberg, Center of Engineering Sciences, Polymer Technology, D-06099 Halle, Germany

ABSTRACT: The electrical resistance of carbon black (CB) filled ethylene-octene copolymer (EOC) was monitored during the compression molding step by means of conductivity sensors. It increases strongly during the cross-linking process due to the de-agglomeration of CB aggregates. After completion of cross-linking reaction CB aggregates reagglomerate causing a decay of resistance. The electrically stimulated shape-memory (SM) behavior was found to be strongly dependent on the extent of electrical resistivity and the rigidity of CB network, which is formed during compounding and subsequent cross-linking process. The effect of amount of peroxide and cross-linking conditions like time and temperature on resistivity and the related SM behavior was characterized. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2138–2145, 2011

Key words: shape-memory behavior; cross-linking; electrical properties

INTRODUCTION

Shape-memory polymers (SMP) are able to recover their predefined original shape when exposed to an external stimulus.[1] They can be thermally stimulated by warming up through a heat source or by applying of a voltage[2,3] or exposed to an infrared radiation,[4] ultraviolet light[5] as well as magnetic field.[6] Recently, thermally induced SM material was developed on the basis of ethylene-octene copolymer (EOC) that is covalently cross-linked by means of peroxide.[7,8] Here, the permanent shape is also fixed by covalent cross-links and the switching process is controlled by the melting temperature of the polyethylene crystallites. Addition of CB into EOC reinforces it and imparts it high electrical conductivity. The electrically stimulated SM effect of EOC filled with different CB types and concentrations has been systematically investigated in our previous work.[9] The SM behavior is strongly dependent on the stiffness of the composites and the extent of the electrical resistivity. It has been also found in our recent work[10] that the conductivity of CB filled EOC and the related SM behavior is very sensitive to the compounding process as well as the obtained CB dispersion and distribution state in the polymer matrix. After compounding CB-filled EOC has been peroxi-dic cross-linked at high temperature for a certain cross-linking time to create a permanent chemical network. It is clear that the material structure (polymer and filler networks) and the related physical properties of the mixtures change in a high manner after the cross-linking process. In the past, some authors[11] reported about a change of resistivity of composites of solution-styrene-butadiene rubber (S-SBR) and CB after vulcanization in a compression molding device. They referred this behavior to a pronounced flocculation/reagglomeration of filler particles taking place in the rubber matrix, which leads to a drastic reduction of resistivity. In contrast, other authors studied the electric conductivity of CB/polyethylene (HDPE)[12–14] and carbon nanotubes (MWNT)/HDPE[15] composites before and after irradiation at different ambient temperatures and found that the resistivity increases significantly after an application of electron or gamma irradiation.

In this work, we installed a sensor system in the compression mold to monitor the change of electrical resistance during the cross-linking process. The structural background of the development of resistance will be discussed by taking into consideration the knowledge reported in literature and our morphological investigation. The impact of the cross-linking process on the electrically stimulated SM behavior will be evaluated.

EXPERIMENTAL

Metallocene-catalyzed homogeneous EOC (Dow Chemical) with ∼ 60 hexyl branches per 1000°C, a

mass-average molecular weight M_w of 87 kg/mol and polydispersity M_w/M_n of 2.5 was used as matrix. A high conductive CB EC600 (Akzo Nobel Chemicals) was used as filler. Its structural parameters, dibutylphthalat number (DBP) of 500 mL/100 g and nitrogen surface area (NSA) of 1400 m^2/g, were given by the provider. Peroxide 2,5-dimethyl-2,5-di(tert.butylperoxy)-hexane (DHBP) (Akzo Nobel Chemicals) was employed as cross-linking agent.

Composites were prepared using a Poly Lab System Rheocord 300 p with a 75 cm^3 mixing chamber Rheomix 610 p (Thermo Haake). The initial chamber wall temperature was kept constant at 60°C for all mixtures, the rotor speed 50 rpm, and the fill factor 0.7. First, EOC and peroxide were mixed for 2 min and then CB was added after 5 min. CB content of 17 wt % was kept constant for all the composites. Different peroxide concentrations were used. The total mixing time of 9 min was chosen to obtain an optimal dispersion degree of CB. To get a clear morphology of CB network formation in the polymer matrix by means of atomic force microscopy (AFM), a reference composite was prepared with the same preparation procedure like the investigated composites. The CB concentration of the reference composite was 4 wt %.

For SM experiments, mixtures were processed after compounding to thin plates with a thickness of 0.5 mm at 110°C and immediately cross-linked at a temperature of 190°C. The cross-linking conditions were varied according to the results received from the online measurement of the electrical resistance to characterize the effect of cross-linking behavior on the structure and related mechanical properties of the composites.

Atomic force microscopy

Morphological investigations were carried out by an atomic force microscope (Quesant Q-Scope 250), operated in intermittent mode. Samples were produced by cutting in a cryo-chamber CN 30 (Microm) with a diamond knife at −100°C.

Offline measurement of electrical resistivity

For the electrical resistivity measurement a multimeter 2750 (Keithley) was used. The shape of the conductive test specimens was a rectangular strip whose ends were coated by silver paste to receive a good contact with the electrodes. Resistivity as a function of temperature was obtained when heating from 30 to 200°C at a heating rate of 5 K/min in an oven. With the same rate the samples were cooled down from 200 to 30°C.

Online measurement of the electrical resistance during the cross-linking process

The mold used for electrical measurement during vulcanization is shown in Figure 1(a). The cavity positioned in the middle of a polyether ether ketone (PEEK) plate had a diameter of 45 mm and a thickness of 2 mm. The electrodes were made from two aluminum foils and insulated from its surroundings by two polytetrafluorethylene (PTFE) foils. A multimeter 2750 (Keithley) was used for measurement of resistance of the composites. The temperature program for pressing and vulcanization is given in Figure 1(b). A pressure of 100 bar was kept constant for the whole pressing process.

Characterization of the SM behavior in bending test

Samples prepared for SM experiments had dimensions of $40 \times 10 \times 0.5$ mm^3 (L × W × T). The SM experiments were performed in bending mode. The samples were wrapped round a metal tube having an outer diameter $d = L/\pi$, and fixed by a duct tape. The wrapped samples were then brought into an oven, which had been heated up to the programming temperature of 90°C. After 5 min tempering in oven samples were taken out and quenched in cool water of 20°C to fix their shape. After this preparation procedure samples having a ring-like shape are programmed and ready for the SM experiments.

When deformed to a ring, the inner layer of the ring is compressed, whereas the outer layer is strained with a deformation $\varepsilon = T\pi/L = 3.93\%$.

For the characterization of the electrically stimulated SM behavior the programmed samples were fixed on an isolating ground by two clamps as described in[9,10] and shown in Figure 2(a). Clamps were connected with a voltage source, and a voltage of 10 V was applied. The sample temperature is increased as a result of the Joule effect. The temperature of the sample was measured using a noncontact temperature measuring device MiniTemp (Neo-Lab). During heating the ring opens and strives to get the permanent shape of a rectangular strip as seen in Figure 2(b).

To quantify the recovery the change of contour of the sample during applying a voltage was analyzed using eq. (1).

$$\text{Recovery} = \frac{\varphi - \varphi_0}{180° - \varphi_0} 100\% \qquad (1)$$

φ_0 is the initial angle determined after programming [Fig. 2(a)]. It characterizes the ability of the composite to fix the temporary shape of the sample. If the crystalline phase of the sample formed during quenching is strong enough to fix the deformation
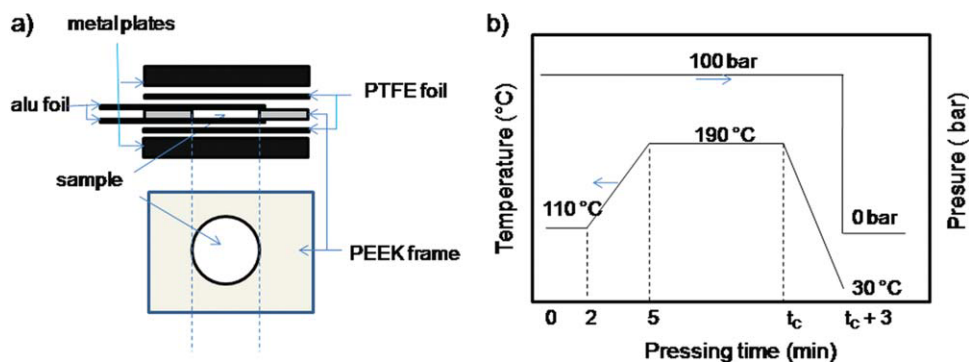
Figure 1 Device for cross-linking and online measurement of electrical resistance (a) and pressing program (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and viscoelastic forces stored in the network efficiently, φ_0 is zero. Otherwise, φ_0 has a certain value, which is determined by the programming temperature and the cross-linking density of EOC as well as the rigidity of the CB network. φ is the angle describing the opening process during heating [Fig. 2(b)]. A 100% recovery is reached when φ reaches 180°.

RESULTS AND DISCUSSION

Temperature dependence of electrical resistivity of CB-filled EOC

To understand the temperature dependent behavior of the investigated composites the change of resistivity of the cross-linked CB-filled EOC during heating and cooling in an oven was measured and is presented in Figure 3 for the first and second heating/cooling run. On heating a decrease of resistivity is observed, which is defined as a negative temperature coefficient (NTC) effect.[16–18] The NTC effect of the investigated sample was observed mainly in the

temperature range above 70°C, in which the crystalline phase of the EOC matrix is completely molten. As temperature increases above the melting point the viscosity is greatly reduced, the mobility of the polymer segments increases, and the flocculation/reagglomeration of CB network is preferably generated, thus a decrease of the resistivity can be observed. The NTC effect is often observed in CB-filled thermoplastics like HDPE in the melt state.[12,16,19-24] Concentration and properties of CB, especially the particle size, are of importance for the temperature characteristics of the resistivity of CB filled rubbers.[25]

At cooling the resistivity of the composite increases as shown in Figure 3. However, it never reaches the value of resistivity before heating. The increasing resistivity with cooling is explained by the reduction of the thermal emission of electrons. The hysteresis of resistivity determined at room temperature is the result of the reagglomeration process of CB particles taking place at high temperatures. In the second heating/cooling run the hysteresis disappears. That may be due to the fact that the
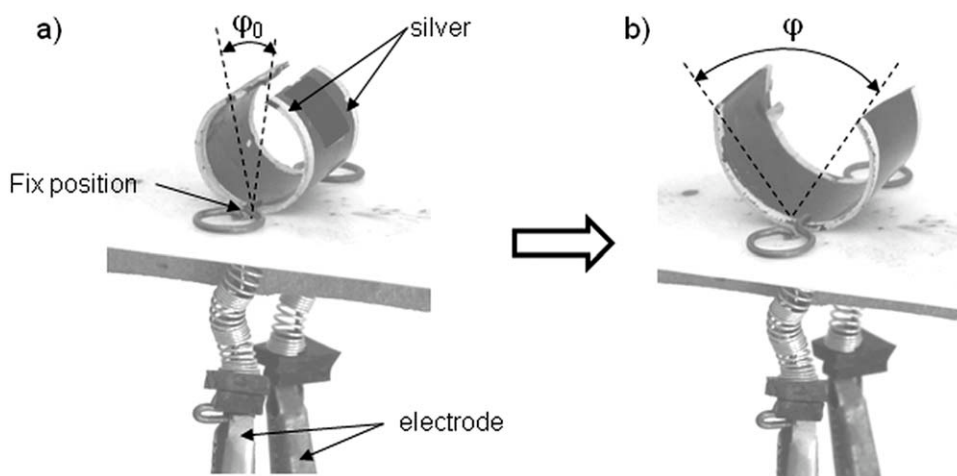

Figure 2 Arrangement of the electrically stimulated SM experiment and quantification of the SM behavior by analysis of the sample contour.
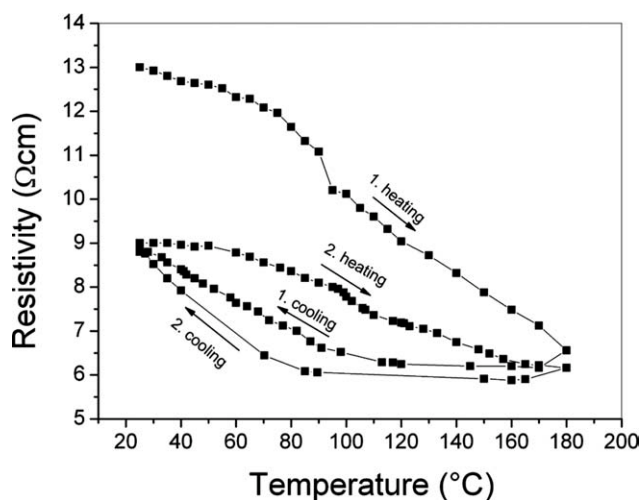
Figure 3 Temperature dependence of resistivity of cross-linked CB-filled EOC composite prepared with 2.5 wt % peroxide at 5 min pressing time and 190°C.

reagglomeration process is already completed after the first run. However, concerning such a behavior questions are raising why and how the reagglomeration process takes place in a vulcanized material and what happened during vulcanizing process with the CB network structure.

Monitoring the change of resistivity during cross-linking process in a compression mold

The change of electrical resistivity of the composites was monitored during the cross-linking process in the compression mold using a conductivity sensor system as described above. The results of resistance measurements [Fig. 4(b)] were compared with the torque-time characteristics obtained from a vulcameter given in Figure 4(a). When the mold temperature reached 170°C at $t_1 = 4$ min, the cross-linking reaction started and as a result the torque increases rapidly up to a maximum value at $t_2 = 7$ min. In this range, during the cross-linking process, the resistance increases from 77 Ω to 280 Ω. Passing t_2, i.e., after the cross-linking process is completed, the torque decreases slightly due to reversion reaction of cross-linking. Meanwhile, the resistance runs through a maximum at t_2 and subsequently decays from 280 Ω to 167 Ω measured at t_3 = 22 min. On cooling to room temperature between t_3 and t_4 the resistance increases rapidly up to a value, which corresponds to the specific resistivity of the composites at room temperature.

The increases of resistance of the composites as a result of cross-linking process in the period between t_1 and t_2 may be correlated with the change of the CB network formation and the structure of the thin polymer layer between the CB aggregates. From the thermodynamic point of view the change of CB network rearrangement during pressing/vulcanizing process can be

explained as illustrated in Figure 5. During the mixing process, under shear stress, rubber molecules are stretched and they infiltrate the filler agglomerates and wet the filler surface. Loss of entropy by stretching means that there is a retractive force for recovery of molecules when external shear stress removed after the mixing process. The polymer contracts into a state of higher entropy, just as if it is driven by an elastic force. When the cross-linking reaction takes place, the entropic force f related to the molecular weight between two chemical cross-links M_C according to the entropy elasticity theory described by eq. (2) and depends on the stretching ratio λ, the density ρ, the Boltzmann constant k and the absolute temperature T[26]:

$$f = (\lambda - \lambda^{-2})\frac{3\rho kT}{M_C^{\text{cross-link}}} \qquad (2)$$

With decreasing $M_C^{\text{cross-link}}$ the entropic force f becomes stronger and can separate the CB aggregates 2 and 3 from the network [Fig. 5(b)]. The deagglomearation of the CB network during the cross-linking process results in an increase of resistivity as observed in Figure 4(b). After the vulcanization process no more new chemical cross-link is formed and
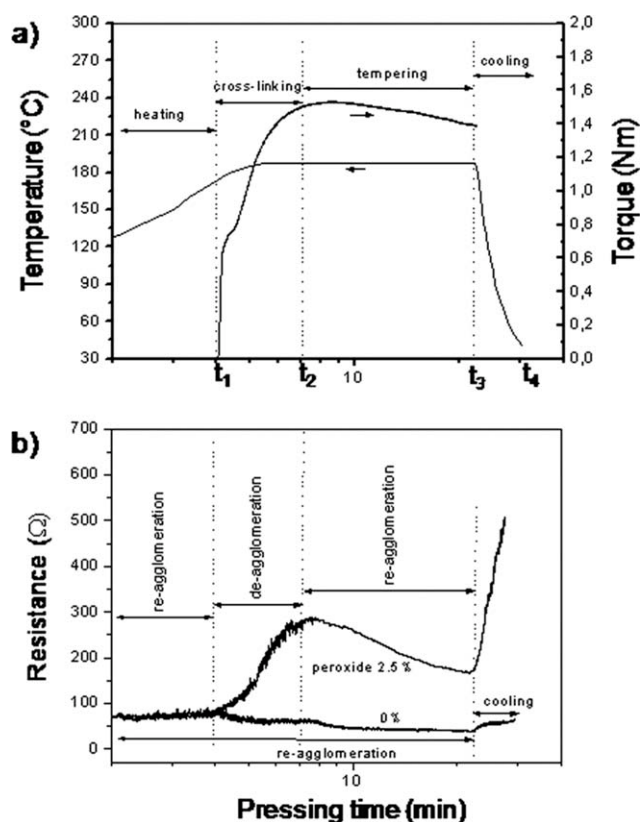

Figure 4 Torque curve received from a vulcameter (a) and electrical resistance change during the cross-linking process monitored in a compression mold (b).
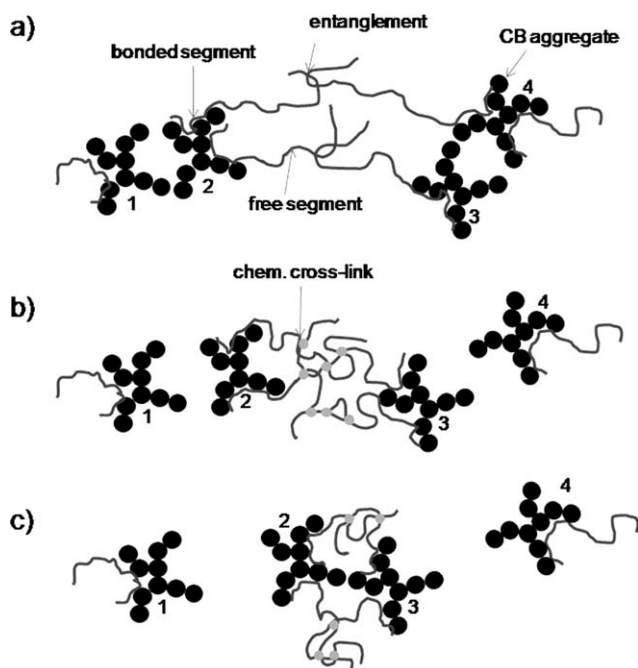
Figure 5 Deagglomeration and reagglomeration of CB aggregates during cross-linking process [after mixing and before cross-linking at t_1 (a), completion of cross-linking reaction at t_2 (b), and after tempering at t_3 (c)].

the entropic force f becomes minimal through the movement of aggregates. In this state the aggregates 2 and 3 are brought together by Brownian motion (reagglomearation) and a new CB network is formed to minimize surface energy as seen in Figure 5(c). As a result the electrical resistivity decreases in the period after cross-linking.

Our morphological investigations of the composites pressed with different time are presented in Figure 6. In the AFM micrograph of the composite pressed up to t_1, when cross-linking process not yet took place, the CB aggregates (white columns) distributed inhomogeneously in the EOC matrix [Fig. 6(a)]. Among those, there are many branch-like CB conductive pathways (marked by dotted lines). These paths run from one CB aggregate to another, forming a conductive network throughout the matrix. In the sample pressed up to t_2 when the cross-linking process is completed CB aggregates are dispersed more uniformly in the matrix and the

agglomeration of the CB aggregates is less pronounced [Fig. 6(b)]. Thus, cross-linking at ambient temperatures causes longer distance between the conductive particles, and as a result, the resistivity increases much higher as before.

The decay of resistance in the period between t_2 and t_3 explained by the flocculation/reagglomeration of CB aggregates due to the heat treatment during vulcanization can be observed in Figure 6(c). Large conductive pathways formed over time by CB agglomeration can be observed clearly. It is also found from the AFM micrographs that the size of the CB aggregates before cross-linking [Fig. 6(a)] and after long pressing time [Fig. 6(c)] is much larger than that of the CB aggregates of shorter pressing time [Fig. 6(b)].

In Figure 4(b) the resistance of CB-filled EOC containing no peroxide was found merely decreasing with pressing time due to the flocculation/reagglomeration of CB aggregates at high temperature.

In literature, some authors[12–14] found that after an application of electron irradiation at room temperature resistivity of thermoplastics filled with CB increases. Xia at el.[12] used the general-effective media (GEM) equation to fit the experimental data of volume fraction dependence of the room temperature resistivity of the CB-filled HDPE composite after irradiation. The parameters in the GEM equation, corresponding to the dispersion character of CB in the HDPE matrix, were determined. The values of the characteristic parameters and the SEM micrographs indicate that aggregates of carbon black constructing a three-dimensional conductive network are oriented along the direction of the electrical field as a result of the irradiation process. The cross-linked polymer matrix, however, is statistically vertical to the electrical current and hinders conductive particles (aggregates) from contacting each other. The hindering effect is more pronounced with higher irradiation doses or at higher ambient temperatures.

The flocculation process was also detected by Meier et al.[11] when investigated the electrical properties of cross-linked and non-cross-linked CB-filled solution-styrene-butadiene rubber (S-SBR) composites. Yu and Baer[27] also observed a time dependent flocculation in the quiescent melt of different thermoplastics filled with CB by atomic force microscopy.
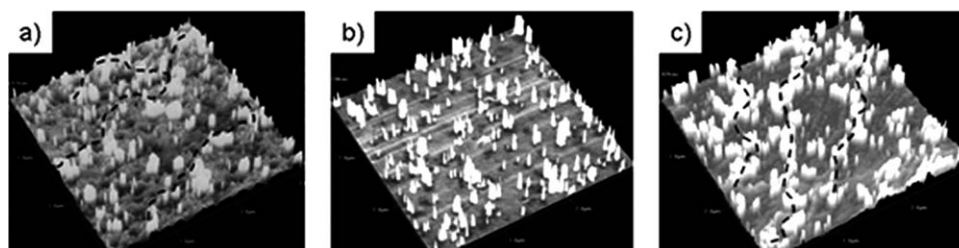

Figure 6 AFM images of cross-linked EOC filled with 4 wt % CB at t_1 (a), t_2 (b), and t_3 (c) (image size 3 μm × 3 μm).
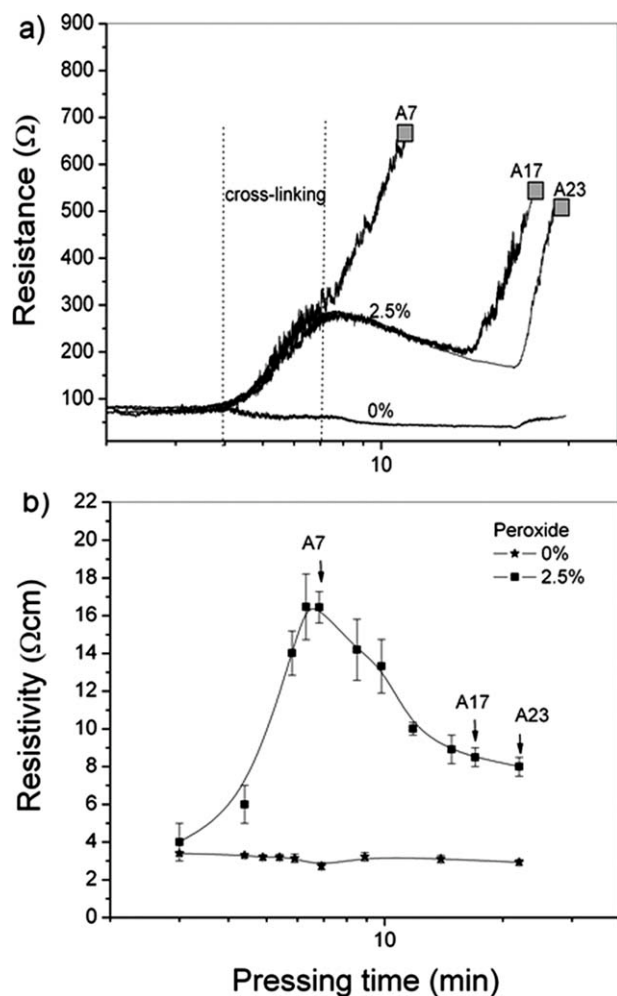
Figure 7 Development of resistance measured directly during the cross-linking process in a compression mold (a) and resistivity of the pressed samples determined from the offline measurements (b).

Effect of cross-linking conditions on the resistivity development and the related SM behavior

Effect of cross-linking time

In Figure 7(a) the resistance of samples pressed with different time t_3 is shown. The offline-value of resistivity of different samples is presented in Figure 7(b).

A very good correlation between the online and off-line values could be observed, i.e., the online measured resistance can be used to monitor the cross-linking process of the CB-filled composites and the development of the electrical properties. Three samples named A7, A17, and A23 with t_3 of 7 min, 17 min and 23 min were chosen for the SM experiment.

Figure 8 presents the SM behavior of the samples A7, A17, and A23. By applying a voltage of 10 V the sample temperature increases differently as seen in Figure 8(a). According to Figure 6(b) sample A7 has the highest resistivity of 16 Ωcm, and as a result it shows the slowest development of temperature. Both samples A17 and A23 with similar resistivity of 8.5 Ωcm show a similar temperature increase. Recovery of the samples determined according to eq. (1) are presented in Figure 8(b) in dependence on the applying time. It is obvious that sample A17 and A23 present the same recovery with increasing applying time because of the same temperature development. Surprisingly, the recovery of the sample A7 does not differ much from the other samples. When presented recovery versus sample temperature as shown in Figure 8(c), it can be seen that sample A7 reaches a recovery of 83% at the temperature 112°C, while the A17 and A23 need to be heated up to 170°C and 185°C, respectively, for the same recovery. To explain the SM behavior, the structure of CB network formed during the pressing process should be taken into consideration. At a short pressing time of the sample A7 CB aggregates were separated [see Fig. 6(b)] because of the cross-linking process as discussed above. Thus, the CB network is not rigid enough and can be recovered at low temperature. Meanwhile, at longer pressing time CB aggregates in samples A17 and A23 reagglomerate to form a rigid network, which can be deformed only at high temperatures. The longer the pressing time, the more rigid is the CB network and the higher the temperature is needed for recovery.

Effect of cross-linking temperature

The effect of temperature on the cross-linking behavior of the CB-filled EOC can be seen in Figure 9(a).
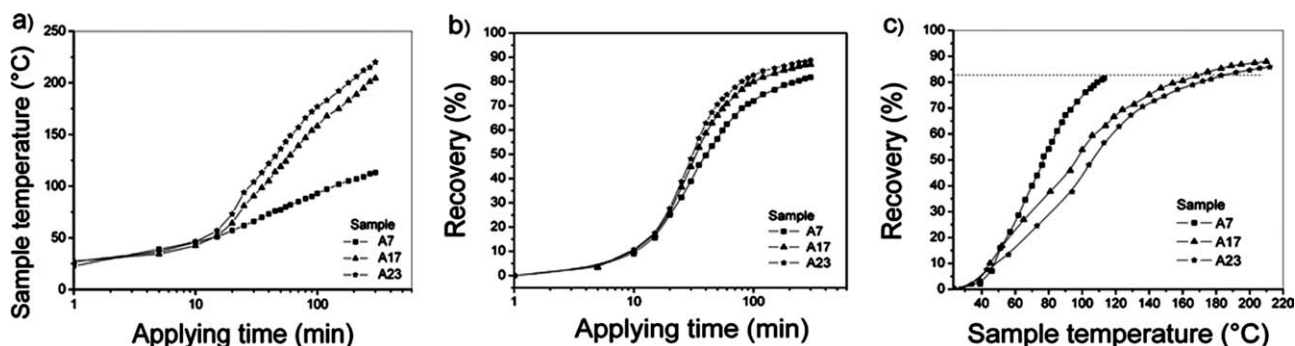

Figure 8 Sample temperature development (a) and recovery in dependence on the applying time (b), and recovery in dependence on the sample temperature (c) (applied voltage 10 V).
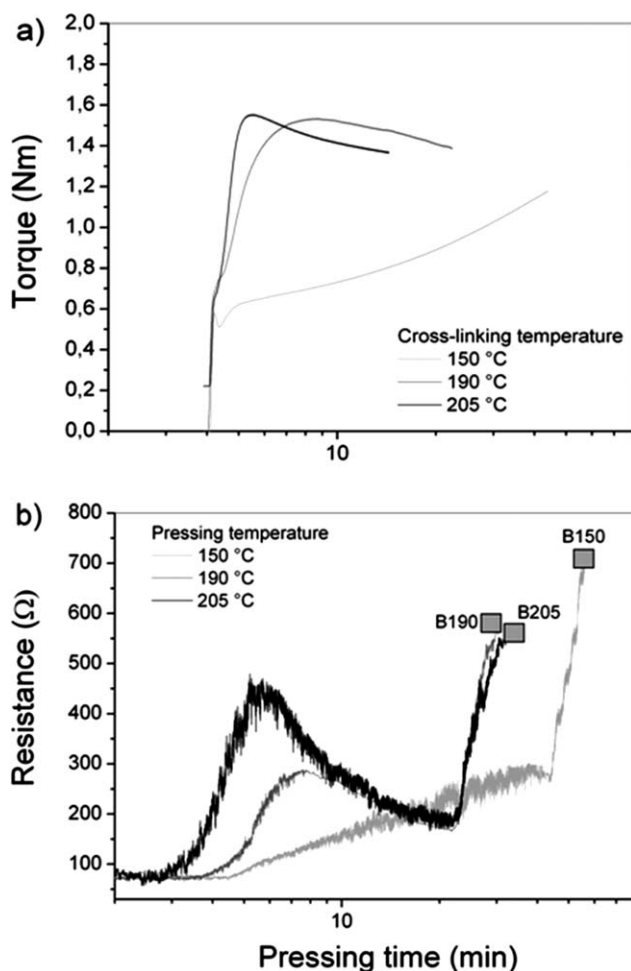
Figure 9　Torque curves received from vulcameter at different temperature (a) and the corresponding resistance received in the compression mold (b).

With increasing temperature the torque curves are shifted to shorter times because of the thermally accelerated reaction of peroxide.

The resistance curves measured in the compression mold at three temperatures are presented in Figure 9(b). Again, a correlation between the cross-linking process and the change of the resistance is obtained for different cross-linking temperatures. Samples B150, B190, and B205 with cross-linking temperatures of 150°C, 190°C, and 205°C were used for the SM experiments.

In Figure 10 the recovery of three samples B150, B190, and B205 is presented in dependence on the sample temperature by applying a voltage of 10 V for a period of 3 min. In sample B190 and B205 the sample temperature increases up to 200°C thank to a low resistivity of 8 Ωcm. Meanwhile, the temperature of sample B150 reaches only 130°C. However, sample B150 could show a recovery of 83% as B190 and B205 at 200°C.

The reason for such a SM behavior is also explained by the CB network formation during the
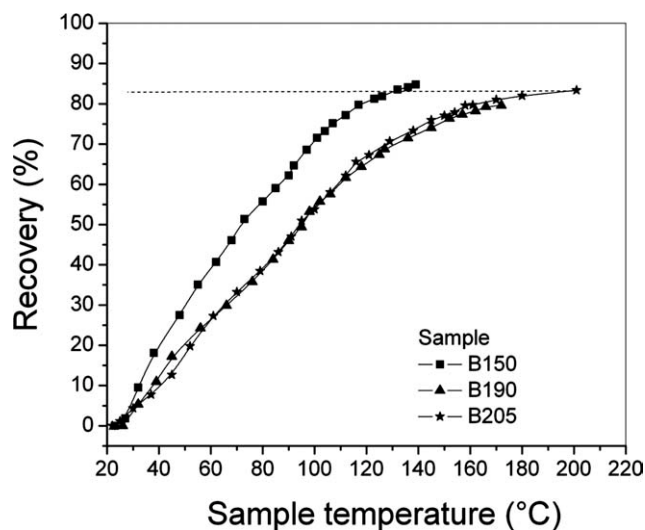
Figure 10　Recovery of samples cross-linked at different temperature in dependence on the sample temperature by applying a voltage of 10 V.

cross-linking process. As seen in Figure 9(b), when the cooling started, the cross-linking process in sample B150 was not yet completed, i.e., that the deagglomeration process still went on. The reagglomeration process in sample B190 and B205 already took place for a period of time. Thus, the rigidity of B190 and B205 is higher than that of B150. Therefore, the recovery of B190 and B205 needs higher temperatures than that of B150.

Effect of amount of cross-linking agent

The change of resistivity with pressing time of samples containing different amount of peroxide is presented in Figure 11. All curves of samples containing peroxide show the typical behavior of resistance with increasing pressing time. However, with increasing peroxide concentration the resistance curves shift to a higher level. Reagglomeration is a
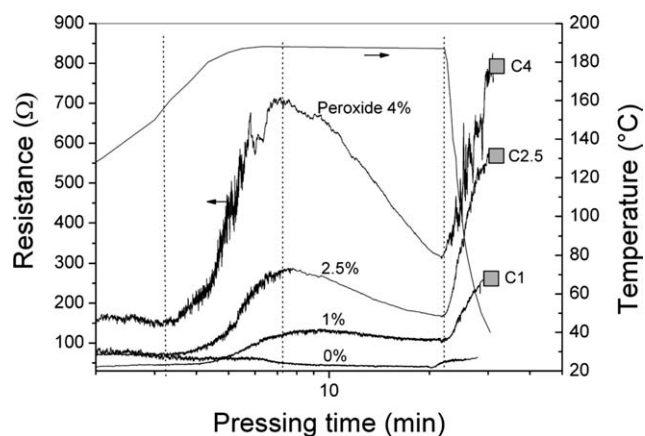

Figure 11　Resistance of samples containing different peroxide concentration in dependence on pressing time.
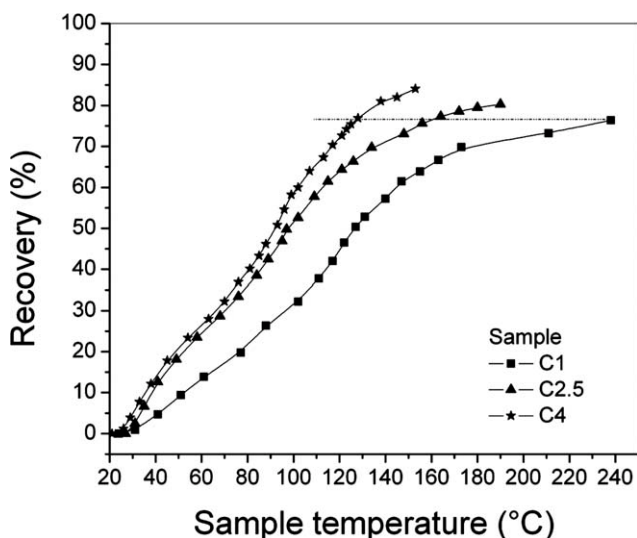
Figure 12 Recovery of samples containing different peroxide concentration in dependence on sample temperature.

diffusion process and, thus, also depends on the viscosity of the matrix polymer. Cross-linking of compounds enhances the matrix viscosity and thus inhibits the rearrangement of the filler particles.[22,24,28,29] After cooling to room temperature, the resistivity of the samples C1, C2.5, and C4 containing 1 wt %, 2.5 wt %, and 4 wt % peroxide, respectively, is 6 Ωcm, 8 Ωcm, and 12 Ωcm, respectively.

The recovery of the samples C1, C2.5 and C4 in dependence on the sample temperature is presented in Figure 12. The high cross-linked sample C4 shows a recovery of 86% at a temperature of 150°C, while the low cross-linked sample C1 reaches a recovery of 75% at a temperature of 240°C. The reason for this behavior is related to the fact that the CB network in C4 is much more destroyed and less reformed than that in the other samples during cross-linking process as seen in Figure 11. Additionally, the extent of the entropic force f being responsible for the recovery process is much higher in sample C4 than in C1 and C2.5. The entropy elastic force is determined by the chemical cross-linking density and thus increased with increasing peroxide concentration.[7]

CONCLUSIONS

The electrical resistivity of cross-linked CB filled EOC was found to be very sensitive to the cross-linking process. A specific sensor installation was applied to characterize the change of resistivity in a compression mold. A typical development of resistance of the composites was found. The resistance increased strongly during the cross-linking process due to the deagglomeration of CB aggregates. After completion of cross-linking CB aggregates reagglomerate causing a decay of resistance. The electrically stimulated shape-memory (SM) behavior is strongly dependent on the extent of electrical resistivity and the rigidity of CB network, which is determined during compounding and subsequent pressing process. The method of the online measured electrical resistance can be used to monitor the cross-linking process and the CB network formation process of CB/polymer composites.

References

1. Lendlein, A.; Kelch, S. Angew Chem Int Ed 2002, 2034, 41.
2. Leng, J. S.; Liu, Y. J.; Du, S. Y. Appl Phys Lett 2007, 91, 144105.
3. Li, F.; Qi, L.; Yang, J.; Xu, M.; Luo, X.; Ma, D. J Appl Polym Sci 2000, 75, 68.
4. Koerner, H. Nat Mater 2004, 3, 115.
5. Lendlein, A.; Jiang, H.; Jünger, O.; Langer, R. Nature 2005, 434, 879.
6. Mohr, R. Proc Natl Acad Sci USA 2006, 103, 3540.
7. Kolesov, I. S.; Radusch H.-J. eXPRESS Polym Lett 2008, 2, 461.
8. Kolesov, I. S.; Radusch, H.-J. Polymer 2009, 50, 5490.
9. Le, H. H.; Kolesov, I.; Ali, Z.; Uthardt, M.; Osazuwa, O.; Ilisch, S.; Radusch, H.-J. J Mater Sci 2010, 45, 5851.
10. Le, H. H.; Ilisch, S.; Uthardt, M.; Kolesov, I. S.; Radusch, H. J Proc Technomer 2009, Chemnitz, Germany, Nov 12-14 2009.
11. Meier, J. G.; Mani, J. W.; Klüppel, M. Phys Rev B 2007, 75, 054202.
12. Xia, J.; Pan, Y.; Shen, L.; Yi, X. S. J Mater Sci 2000, 35, 6145.
13. Jia, W.; Chen, X.; Li, S. J Appl Polym Sci 1996, 60, 2317.
14. Kang, P. H.; Nho, Y. C. J Ind Eng Chem 2001, 7, 199.
15. He, X. J.; Du, J. H.; Ying, Z.; Cheng, H. M. Appl Phys Lett 2005, 86, 062112.
16. Chen, X. B.; Issi, J. B.; Cassart, M.; Devaux, J.; Billaud, D. Polymer 1994, 35, 5256.
17. Balta Calleja, F. J.; Ezquerra, T. A.; Rueda, D. R.; Alonso-Lopez, J. J Mater Sci Lett 1984, 3, 165.
18. Al-Allak, H. M.; Brinkman, A. W.; Woods, J. J Mater Sci 1993, 28, 117.
19. Fournier, J.; Boiteux, G.; Seytre, G.; Marichy, G. J Mater Sci Lett 1997, 16, 1677.
20. Aneli, D. N.; Topchishvili, G. M. Int Polym Sci Technol 1986, T/91, 13.
21. Zhang, M.; Jia, W.; Chen, X. J Appl Polym Sci 1996, 62, 743.
22. Tang, H.; Piao, J.; Chen, X.; Luo, Y.; Li, S. J Appl Polym Sci 1993, 48, 1795.
23. Narkis, M.; Vaxman, A. J Appl Polym Sci 1984, 29, 1639.
24. Sherman, R. D.; Middleman, L. M.; Jacobs, S. M. Polym Eng Sci 1983, 23, 36.
25. Zhang, J.; Feng, S. J Appl Polym Sci 2003, 90, 3889.
26. Treloar, L. R. G. The Physics of Rubber Elasticity, 3rd ed.; Oxford: Clarendon Press, 1975.
27. Yu, J.; Zhang, L. Q.; Rogunova, M.; Summers, J.; Hiltner, A.; Baer, E. J Appl Polym Sci 2005, 98, 1799.
28. Meyer, J. Polym Eng Sci 1973, 13, 462.
29. Voet, A. Rubber Chem Technol 1981, 54, 42.