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Combination of a Viscoelastic and a Tribological Analysis of a Low-Density Polyethylene with a High Degree of Cross-linking

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Cross-linking of polymers is an efficient method to tailor the end-use properties of polymer materials. Cross-linking using a chemical agent, e.g., dicumyl peroxide (DCP), allows for a spatially uniform network formation in the melt state. In addition, it is also associated with side reactions which influence the final properties of the plastic part. This work investigates the influence of DCP concentration on the tribological properties of a cross-linked low-density polyethylene (LDPE) grade. In particular, high DCP concentrations up to 20 phr are chosen in order to explore the effect of a high degree of cross-linking. The viscoelastic properties below and above the melting temperature are studied in detail to support the interpretation of the tribological results. Rheological investigations allow one to monitor the cross-linking of the long-chain branched LDPE. The data and the subsequent optical analysis show that wear already is significantly reduced at a low DCP concentration of 1 phr because of the covalent bonds caused by cross-linking. A high DCP concentration of 20 phr yields an increase of coefficient of friction which can be explained by the low stiffness and the resulting high contact area in the case of highly cross-linked LDPE.

1. Introduction

The molecular structure of polymer materials essentially determines the final properties of plastic products. For example, chemical cross-linking strongly influences the viscoelastic and tribological properties of homopolymers. An important commodity thermoplastic polymer is polyethylene which can be cross-linked to very high degrees by γ-irradiation.[1] This greatly improves the resistance to abrasion of this polymer, which is of great importance, for example in hip implants. Since γ-irradiation is elaborate due to the required safety protocols, chemical cross-linking has a broader applicability. A typical chemical cross-linker is dicumyl peroxide (DCP).[2,3] In contrast to cross-linking by means of irradiation, not only the surface of the plastic part is altered, but also the bulk part of the polymer. By means of network formation, a variety of properties are enhanced, e.g., thermal stability (increase of heat distortion temperature), chemical resistance (decrease of solubility), and water tree aging.[4] Furthermore degradation is also influenced by cross-linking.[5] However, the byproducts caused by side reactions during cross-linking also influence the properties of the final part.[6] The effect of processing variables of a low-density polyethylene (LDPE) for low DCP concentrations was investigated.[2] Already at a low DCP concentration of 1.5 wt% a high gel fraction (above 84 wt%) can be achieved. Whereas the gel fraction itself only gives a limited insight into the molecular structure, a morphological analysis of cross-linked LDPE gives additional information on molecular properties.[7] At low DCP concentrations, spherulites were determined by means of scanning electron microscopy. At higher DCP concentrations, axialities and random-like crystals were observed in the samples with a maximum DCP concentration of 7 wt%.[8] Furthermore, the size of the crystalline domains decreases with increasing DCP concentration.

Cross-linking can also affect the tribological properties of polymers as shown by irradiation of ultra-high molecular weight polyethylene.[9] A few works investigated the influence of cross-linking on the tribological properties of polymers. In the work of

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Künkel et al., the effect of radiation cross-linking of polyamide 6.6 was studied.[10] A number of studies focused on the wear properties of linear polyethylenes such as high-density polyethylenes and ultra-high molecular weight polyethylenes. A comprehensive study on the tribological properties of a high-density polyethylene has been performed by Molinari et al.[11] The study of Molinari et al. showed that the wear rate can be reduced by cross-linking.[11] On the contrary, the tribological properties of branched polyethylenes (such as LDPE) have been investigated to a much lesser extent. It is worth to be mentioned that the improvement of tribological properties is not sufficient for engineering applications. Simultaneously, the mechanical properties need to be maintained on a high level for applications. Whereas the mechanical properties have been investigated by several authors, a correlation between mechanical, rheological, and tribological properties is still missing.

The mechanical properties of cross-linked polyethylenes were studied in several publications. Khonakdar et al. analyzed the properties of a cross-linked high-density polyethylene which is the linear counterpart of long-chain branched LDPE.[12] The authors used *tert*-butyl cumyl peroxide (BCUP) for cross-linking. In their work, the mechanical properties were also determined at different temperatures. The tensile tests revealed the change from a ductile to a rubbery behavior for cross-linked polyethylenes when exceeding the melting temperature. However, the tribological properties were not studied by the authors. The authors investigated the influence of cross-linking on shrinkage.[13] The tensile properties were also investigated in their work. In addition, a linear relation between strain at break and the molecular weight between two cross-links was observed. However, no rheological and tribological tests were performed, either. In summary, in these mentioned works the mechanical properties were studied in detail, however in most cases up to 3 phr peroxide. In addition, no correlation with the tribological properties has been established.[14]

Rheological investigations of cross-linked polyethylenes were performed.[15] The sol and gel fractions were extracted from cross-linked LDPE samples and investigated separately. The authors applied the theory of Winter et al.,[16] to the analysis of the dynamic moduli G' and G'' as well as the relaxation modulus $G(t)$. The data clearly show that a DCP concentration of 1 phr is sufficient for formation of a complete network. However, the maximum DCP concentration in their work was 2 phr and thus still in a regime of low concentrations. The Flory–Rehner approach was applied for calculation of the molecular weight between two cross-links instead of using rheological data.

Generally, most previous works were limited to low DCP concentrations and did not correlate viscoelastic and tribological properties. In this work, we focus on a LDPE which can be processed at a lower temperature than high-density polyethylene. Because of the lower processing temperature, DCP is chosen as cross-linking agent. By varying the concentration of the cross-linking agent, the degree of cross-linking of polyethylene is systematically varied. The objective of this work is to investigate the effect of cross-linking on mechanical, rheological, and tribological properties and to elucidate the interrelation between molecular structure and end-use properties, in particular the tribological properties. In contrast to previous publications, the effect of high DCP concentrations (much larger than 3 phr than in most studies) has been investigated. Using rheological methods, the cross-linking reaction is studied. The mechanical properties are investigated in order to interpret the local deformation during the tribological experiments which were carried out using a ball-on-disc tribometer.

2. Experimental Section

2.1. Materials and Sample Preparation

A commercial LDPE (Lupolen 1840 D, LyondellBasell Industries, Rotterdam, The Netherlands) with a density of 0.912 g cm^{-3} (room temperature, measured using a pycnometer) was chosen for the investigations. Generally, LDPE is classified as long-chain branched. The cross-linking agent was DCP, which was purchased from Sigma-Aldrich (Saint Louis, MO, USA). The repeating unit of polyethylene and the chemical structure of DCP are displayed in **Figure 1**. **Table 1** lists some physical properties of these materials.

Polyethylenes with different DCP concentrations were prepared by extrusion on a micro-compounder (Twin-Screw Mini-Extruder 3.5 ccm, DSM Research, Sittard, The Netherlands) for 5 min at a temperature of 122 °C. This processing temperature (below the so-called safe processing temperature $T_2 = 130\ ^{\circ}\mathrm{C}$ of DCP) was low enough to suppress (or more precisely to delay) cross-linking to a large extent. After extrusion the pelletized extrudates were stored in a refrigerator at a temperature of 10 °C for a few days at maximum. The cross-linking reaction was carried out during compression molding of the extrudates at a temperature of 160 °C which yields a higher reaction speed. A commercial press 63 TC (Hidralmac Europe GmbH, Ennepetal, Germany) was used for sample preparation. The time of compression molding was 30 min. This time interval was sufficient to attain a complete cross-linking at 160 °C.[2] The geometry of the molds was chosen according to the different types of tests (mechanical, rheological, and tribological experiments). The following fractions of DCP were chosen and are given in parts per hundred rubber (phr): 1, 2, 3, 4, 10, and 20 phr. The pristine LDPE was processed under the same conditions as the mixtures. After compression molding, the samples cross-linked with DCP concentrations below and above 10 phr were stored in a vacuum chamber at a temperature of 50 °C and 70 °C, respectively, to remove byproducts of the cross-linking reaction such as acetophenone.

At elevated temperatures DCP can disintegrate into two radicals which finally initiate via a homolytic separation of hydrogen atoms cross-linking of polyethylene chains. In the work of Sahyoun et al.,[6] it has been shown that a variety of byproducts can be created. Note that in general byproducts of a low molar mass can efficiently alter the viscoelastic properties.[17]

2.2. Thermal and Rheological Experiments

The thermal properties of pristine LDPE and the cross-linked samples were determined by means of a differential scanning calorimeter DSC 8500 (PerkinElmer Inc., Shelton (CT), USA).

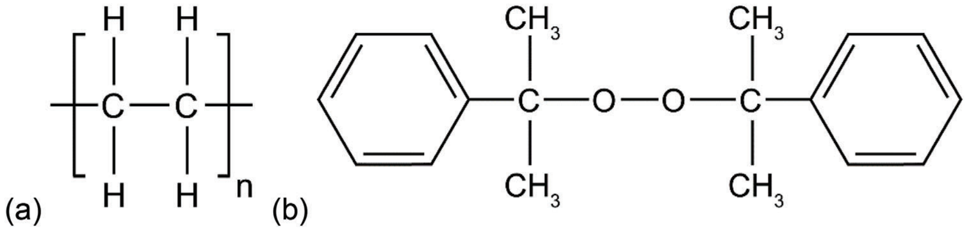

Figure 1. Chemical structures of a) polyethylene and b) dicumyl peroxide (DCP).

The mass of the samples was approximately 5 mg. The measurements were performed in a nitrogen atmosphere. The heating and the cooling rates were both 10 K min^{-1}. The temperature range was 0 °C to 150 °C. For the calculation of the crystallinity the melting enthalpy value $\Delta H_{\mathrm{m}}^{0} = 293\ \mathrm{J\ K}^{-1}$ was chosen.[18] At least three tests were performed for each DCP concentration. Then the degree χ_{c} of crystallinity was calculated using

$$\chi_{\mathrm{c}} = \Delta H_{\mathrm{m}} / \Delta H_{\mathrm{m}}^{0} \tag{1}$$

based on the measured melting enthalpy ΔH_{m}.

For the rheological experiments, cylindrical samples with a thickness of 1 mm and a diameter of 25 mm were prepared by compression molding. Uncross-linked samples which also contained DCP were prepared by compression molding at a lower temperature of 120 °C and a shorter compression time of 6 min. A stress-controlled rotational rheometer (Kinexus Ultra+, Netzsch, Selb, Germany) was used in this study for the rheological experiments. After insertion of the cross-linked samples, a time interval of 10 min was chosen for thermal equilibration. The measurement gap was carefully set such that the normal force on the sample was in the range of 2 to 5 N leading to a complete contact between plates and sample. In order to determine the linear viscoelastic range, amplitude sweeps at an angular frequency ω of 0.10 rad s^{-1} were carried out first. Frequency sweeps were performed in the range of angular frequencies from 0.01 to 100 rad s^{-1} (starting with the highest frequency) with a stress amplitude in the linear viscoelastic regime. Timesweeps with a shorter time of temperature equilibration were also carried out at an angular frequency of 0.10 rad s^{-1}.

Temperature sweeps under uniaxial loading were performed using a testing device DMA 850 (TA Instruments, Eschborn, Germany). The samples with a width of 10 mm were cut from cylindrical specimens for rheological tests. The pretension was 0.2 N. The frequency was 1 Hz, which corresponds to an angular frequency of $\omega = 6.28$ rad s^{-1}. The temperature range was 30 °C to 200 °C with a heating rate of 5 K min^{-1}.

Table 1. Properties of the low-density polyethylene (LDPE) grade Lupolen 1840 D (LyondellBasell Industries) and dicumyl peroxide (DCP; Sigma-Aldrich) according to the supplier.

Material	Molar mass [g mol^{-1}]	T_{m} [°C]	T_{c} [°C]
LDPE	20 000 (M_{n}) 470 000 (M_{w})	110	97
DCP	270.4	39–41	39–41

2.3. Mechanical and Tribological Experiments

The mechanical properties of uncross-linked (pristine) and cross-linked LDPEs were investigated by means of tensile tests under uniaxial loading. A universal testing device AG-XD plus (Shimadzu Corp., Kyoto, Japan) was used for the investigations. The measurements were performed in a temperature-controlled laboratory at 23 °C. Samples of type ISO 527-2/1BA were prepared by compression molding. After annealing at a temperature of 50 °C and 70 °C, respectively, the specimens were used for the investigations. The Young´s modulus E was determined at a strain rate of $\dot{\varepsilon}_t = 1\%\ \mathrm{min}^{-1}$ in the strain interval of 0.05 – 0.25%. Then the samples were unloaded and subsequently elongated again with a rate of $\dot{\varepsilon}_t = 50\%\ \mathrm{min}^{-1}$ for the evaluation of the complete stress–strain curve. Five specimens were tested for each DCP concentration.

Tribological tests with a ball-on-disc tribometer THT (Anton Paar TriTec SA, Graz, Austria) were also performed. The ball material was steel of type 100Cr6 with a diameter of 6 mm and a hardness of (11.3 ± 0.2) GPa. The tribological experiments were carried out at room temperature in normal ambient atmosphere. For the tribological tests, cylindrical specimens with a diameter of 40 mm and a thickness of 2 mm were used. The coefficient of friction μ is defined by

$$\mu = F_{\mathrm{R}} / F_{\mathrm{N}} \tag{2}$$

The friction force F_{R} was measured by the tribometer, and the applied normal force F_{N} was set to 5 N. The velocity of the sphere was 10 cm s^{-1} which corresponds to 95.4 revolutions per minute. The value of μ was determined in the linear regime after the run-in period. The criterion for termination of the tribological tests was a total path s of 400 m. The wear rate k is given by

$$k = W_{\mathrm{V}} / \left(F_{\mathrm{N}} \times s \right) \tag{3}$$

with the wear volume W_{V} and the sliding path s. The value of W_{V} was optically measured. Four samples were tested for each DCP concentration.

The surface of the samples was evaluated using a 3D profilometer (InfiniteFocus, Alicona Imaging GmbH, Raaba, Austria) for the determination of the wear volume W_{V}. Slices at four positions on the surface of the sample were selected for the optical investigations. Then the wear volume W_{V} was determined by means of an image analysis software IFM 2.2 (Alicona Imaging GmbH).

All compression-molded samples of uncross-linked and cross-linked LDPE were dried in a vacuum chamber before the exper-

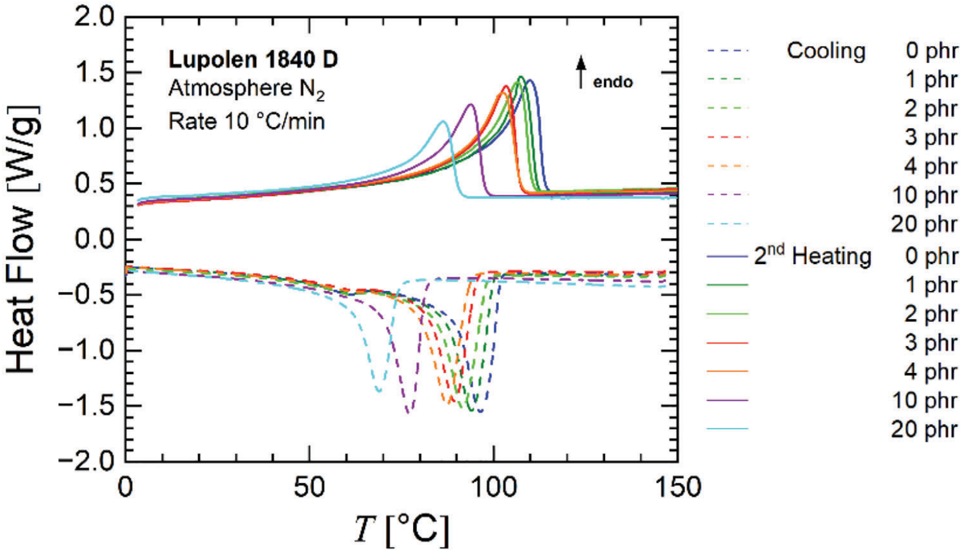

Figure 2. Heat flow for uncross-linked and cross-linked low-density polyethylene (LDPE) vs. temperature T as determined by DSC experiments. The dicumyl peroxide (DCP) concentration is indicated.

iments at a temperature of 50 °C (0 to 4 phr) and 70 °C (10 and 20 phr) for 2 weeks. Mass sorption experiments verified that this drying time was sufficient.[6]

3. Results and Discussion

3.1. Thermal and Rheological Properties

The DSC investigations allow determination of thermal transitions and the degree of crystallinity. The results of the DSC measurements are depicted in **Figure 2** which presents the second heating and the cooling curve for the investigated range of DCP concentrations. The DSC diagrams clearly reveal the melting and the crystallization peaks. LDPE shows a broad melting peak with a peak temperature at 110 °C and a crystallization peak at 97 °C. With higher DCP content (i.e. higher degree of cross-linking) the melting and the crystallization peaks and the end of the melting/onset of crystallization shift to lower temperatures. In addition, the melting enthalpy decreases with higher DCP concentration. Consequently, the degree of crystallinity shows the same behavior, see Equation (2). These trends are quantitatively shown in **Figure 3**. In particular, no converging, limiting behavior can be seen in the concentration range up to 20 phr. The formation of chemical cross-links hinders crystallization of the LDPE chains and yields a decreasing size of lamellae with higher degree of cross-linking. The decrease of the size of crystallites in cross-linked LDPE was also confirmed by wide angle X-ray scattering.[19] The Gibbs–Thomson equation[20]

$$T_{m,\text{peak}} = 414.2\ \text{K} \times (1 - 0.627\ \text{nm}/d) \qquad (4)$$

allows to estimate the average size d of lamellae using the temperature of the melting peak $T_{m,\text{peak}}$. Calculation based on the lowest and the highest peak melting temperature shows that the calculated thickness of the lamellae ranges between 4.7 and 8.3 nm.

Rheological studies are a powerful tool in order to get insight into the cross-linking reaction. Rheological data allow the determination of the time scale and the degree of cross-linking of the LDPE samples after processing. The time-dependence of the cross-linking reaction was monitored using initially uncross-linked samples in a timesweep with constant angular frequency and amplitude, see **Figure 4**. The cross-linking reaction is associated with the appearance of byproducts of low molar mass. These byproducts and possible chain scission as a side-reaction might cause a plasticising effect and tend to decrease the melt viscosity. The constant values of the dynamic moduli indicate that uncross-linked LDPE is stable under these measurement conditions. The comparison of the uncross-linked and cross-linked LDPE shows that the storage modulus G' of cross-linked LDPE increases with time t because of cross-linking until an almost stationary value at a time of approximately 20 min is achieved. Thus, the cross-linking reaction is terminated after approximately 20 min which is in agreement with the work of Gulmine and Akcelrud.[2]

Shear oscillations in the linear viscoelastic regime were carried out to probe the material response at different time scales as well as to determine the molecular weight between cross-links. The data of the dynamic moduli G', G'' and the loss tangent $\tan\delta = G''/G'$ are shown in **Figure 5**. The dynamic moduli of uncross-linked LDPE correspond to the cross-over from the rubbery to the terminal zone. The cross-over of the storage and loss moduli falls in the frequency range which was accessible in the rheological experiments. However, the terminal zone with the characteristic power laws $G' \propto \omega^2$, $G'' \propto \omega$ is not completely achieved.

The cross-linked LDPE samples depict a completely different viscoelastic behavior than the uncross-linked LDPE already at a low DCP concentration of 1 phr. A clear monotonic trend can be seen in Figure 5a,b. The data for the cross-linked LDPE samples with 1 and 2 phr DCP show the characteristic power laws $G' \propto \omega^m$, $G'' \propto \omega^n$.[16] The loss modulus decreases with increasing DCP concentration, which indicates the transition to a solid-like material. At DCP concentrations of 10 and 20 phr the

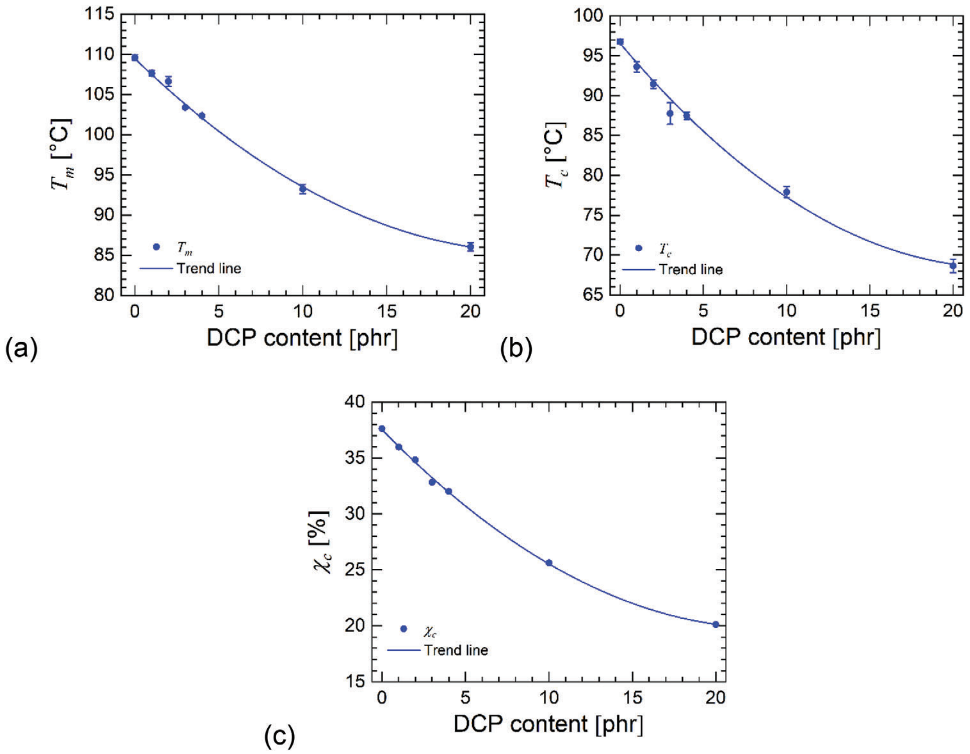

Figure 3. Results of analysis of DSC data: a) Melting temperature T_m, b) crystallization temperature T_c, and c) crystallinity χ_c as a function of dicumyl peroxide (DCP) concentration.

values of G'' are associated with larger experimental scatter (resulting from the very low loss tangent) and thus are not shown. The values of the power-law exponent m decreases with DCP concentration, see **Table 2**. The storage modulus is frequency-independent for a high DCP concentration because of a pronounced elastic behavior. The loss tangent tan δ of the cross-linked LDPE is smaller than unity, which shows that a so-called infinite network is formed. The analysis of our frequency sweeps reveals that a higher degree of cross-linking causes a larger storage modulus and—as revealed by the theory of rubber elasticity—reduces the molecular weight between cross-links. In summary, our rheological data indicate a successful cross-linking reaction which yields a larger number of cross-links with increasing DCP concentration. The degree of cross-linking proceeds monotonically with higher DCP concentration.

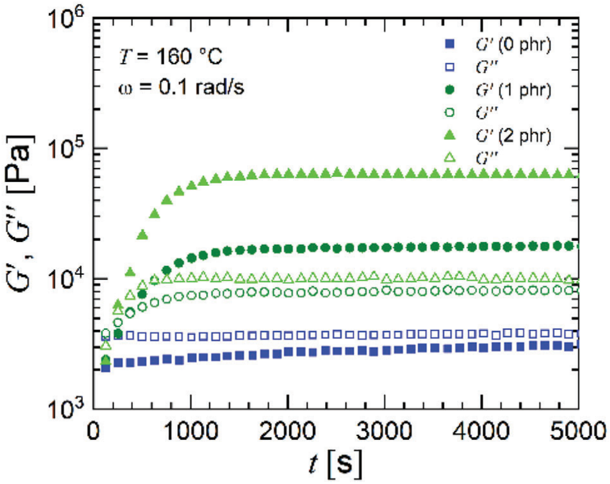

Figure 4. Dynamic moduli $G'(t)$, $G''(t)$ measured in timesweeps on an initially uncross-linked low-density polyethylene (LDPE)/dicumyl peroxide (DCP) mixture at an angular frequency of $\omega = 0.1$ rad s^{-1}. The shear amplitude was 1%.

The increase of G' is caused by the covalent network and the reduction of G'' can be explained by hindrance of movements of the polyethylene segments (reptation of the complete chain) on long length scales. Comparison with the gel content in previous works reveals that a high DCP concentration effectively reduces the average molecular weight between cross-links, while a residual sol content in the order of a couple percent still exits.[21]

Furthermore, temperature sweeps in the tensile mode were performed in order to determine the degree of cross-linking. **Figure 6** presents the storage modulus E' as a function of temperature T for uncross-linked and cross-linked LDPE samples. The overall behavior is in agreement with the results of the DSC and the rheological experiments in shear. The molecular weight M_c between cross-links can be calculated by measuring the tensile modulus E_{network} of the network[22]

$$E_{\text{network}} = 3\varrho RT/\left(M_c\right) \tag{5}$$

with the universal gas constant R. The density ρ at 160 °C was calculated.[23] The value of E' at a temperature of 160 °C was used to calculate M_c using Equation (5). A linear trend for E' in dependence on the DCP concentration is clearly seen in **Figure 7a**.

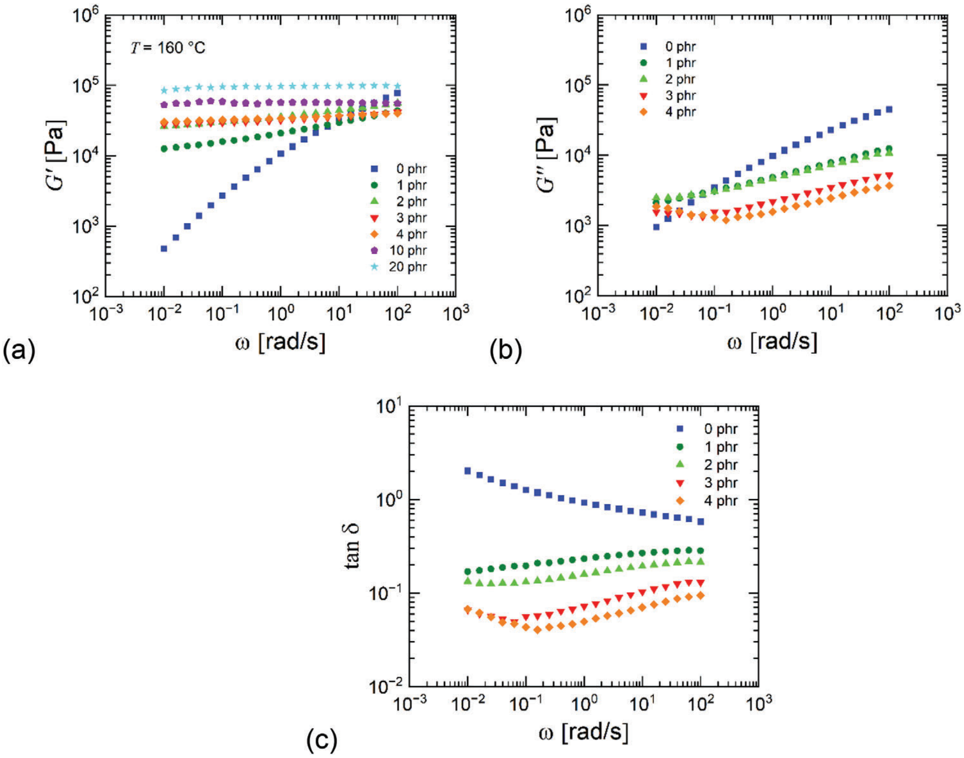

Figure 5. Dynamic moduli $G'(\omega)$, $G''(\omega)$ measured in frequency sweeps at a temperature of 160 °C. a) Storage modulus G'. b) Loss modulus G''. c) Loss tangent $\tan\delta$.

Furthermore, for these cross-linked polyethylenes the value of M_c seems to approach the entanglement molecular weight M_e = 828 g mol^{-1} at high DCP concentrations (Figure 7b). Note that different sources give slightly higher values of M_e.[24] The change of the viscoelastic behavior of cross-linked polyethylene because of melting of the crystalline domains can be also seen in tensile tests which are performed at different temperatures.[13] Above the melting temperature of the cross-linked LDPE, the cross-linked specimens behave rubbery.

3.2. Mechanical and Tribological Properties

The results of the tensile tests under uniaxial loading are presented in **Figures** 8 and 9. In Figure 8, the nominal stress σ_t is presented as a function of nominal strain ϵ_t. The stress–strain curves depict a clear trend as a function of DCP concentration. The curve for pristine LDPE depicts two yield points, a necking and finally hardening. The wide-angle X-ray scattering experiments showed that this double yielding phenomenon is associated with partial melting and recrystallization of the crystallites.[26] At a low DCP concentration (up to 2 phr), an increasing degree of cross-linking

Table 2. Power law exponent m as obtained by analysis of the storage modulus $G' \propto \omega^m$ for the low-density polyethylene (LDPE) samples of this study.

DCP concentration [phr]	m [–]
0	0.76 ± 0.01
1	0.14 ± 0.00
2	0.08 ± 0.00
3	0.04 ± 0.00
4	0.03 ± 0.00
10	0.00 ± 0.00
20	0.01 ± 0.00

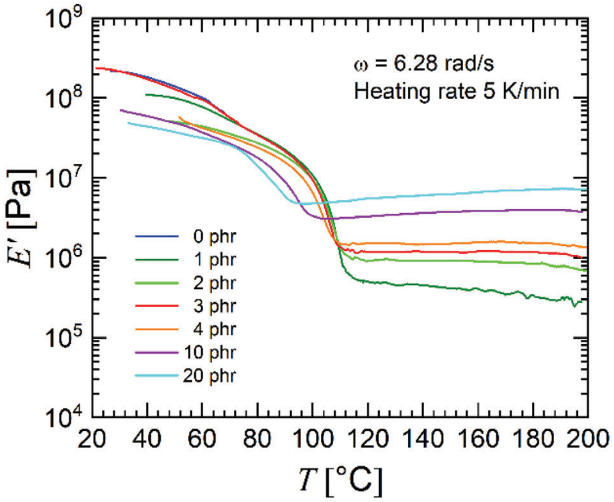

Figure 6. Storage modulus E' as a function of temperature T as determined by dynamic mechanical experiments in the tensile mode. The frequency was 1 Hz ($\omega = 6.28$ rad s^{-1}, respectively). The dicumyl peroxide (DCP) concentration is indicated.

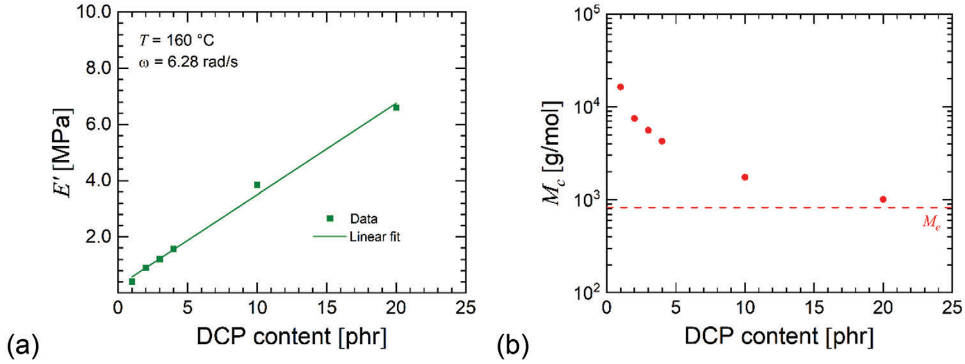

Figure 7. a) Storage modulus E' and b) average netchain molecular weight M_c between two cross-links as a function of dicumyl peroxide (DCP) concentration as determined by the temperature sweeps in the tensile mode. The dashed line in (b) is the value of the entanglement molecular weight M_e = 828 g mol^{-1} taken from elsewhere.[25]

yields a higher stress $\sigma_{t,b}$ at fracture. At higher DCP concentrations than 2 phr, the stress at fracture decreases. On the contrary, the strain $\epsilon_{t,b}$ at break monotonically decreases with increasing degree of cross-linking. In fact, cross-linking with a large DCP concentration causes embrittlement of LDPE.

Figure 9 depicts the results of evaluation of the mechanical properties. The Young´s modulus E decreases with higher degree of cross-linking (Figure 9a) as already revealed by the DMA experiments. The Young´s moduli measured by tensile testing and DMA are in good agreement. This trend can be explained by the decrease of crystallinity with increasing DCP concentration, see Figures 2 and 3. The strain at break also monotonically decreases with DCP concentration (Figure 9b). Similar to the work of Zhang et al.[14] the strain at break linearly depends on M_c, which was determined in this work by rheological methods, see the inset of Figure 9b. The random, covalent network hinders large mechanical deformations, which cause failure at low strain values for high DCP concentrations. At high DCP concentrations the cross-linked LDPE behaves very brittle at room temperature. The stress at fracture shows a maximum at a DCP concentration of 2 phr, see Figure 9c. This maximum is the result of the superposition of the increase of restoring force at large deformations (caused by the stretched covalent bonds in the cross-linked samples) and the decrease of strain at break with DCP concentration. Since mostly nominal stress increases with nominal strain, a lower strain at break is generally associated with a lower stress at break. The superposition of both effects causes the maximum of $\sigma_{t,b}$.

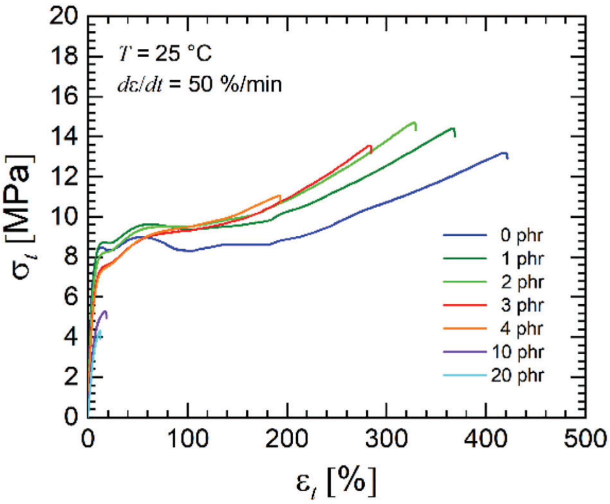

Figure 8. Nominal stress σ_t as a function of nominal strain ϵ_t at room temperature. The nominal strain rate was $\dot{\epsilon}_t = 50\%\ min^{-1}$.

The tribological behavior of the LDPE/100Cr6 pair is the result of the property of the complete tribological system. **Figure 10a** presents the coefficient of friction μ and the wear rate k at room temperature. The coefficient of friction of pristine LDPE attains a value of 0.51 ± 0.02 which is in agreement with literature data.[27] A photograph in Figure 10c shows an LDPE transfer layer on the steel sphere which results from the abrasive wear and causes a self-lubricating effect. Our data clearly show a monotonic increase of the coefficient of friction with increasing DCP concentration (Figure 10a). In particular, at a DCP concentration of 20 phr the coefficient of friction is larger than unity. Cross-linking by means of peroxide decreases the crystallinity and thus the stiffness of the LDPE specimens. Consequently, the applied normal force causes a larger compressive deformation of the cross-linked specimens with increasing DCP concentration and thus a larger contact area. This effect yields an increase of coefficient of friction with higher DCP concentration.

Figure 10b presents the measured values for the wear rate k. Even at a DCP concentration of 1 phr the wear rate is remarkably reduced in comparison to pristine LDPE because of the covalent bonding. The relative wear reduction is approximately 37%, but the method becomes more reliable at DCP concentrations of 4 and 10 phr and the average k value is lowered to less than 25% of that of pristine LDPE. Our data reveal that a higher DCP concentration does not significantly reduce the wear rate. This result implies that already a limited number of cross-links efficiently decreases the abrasive wear at the chosen test parameters, but higher DCP concentrations seem to result in more homogeneously cross-linked materials. At a DCP concentration of 20 phr only a tiny layer of LDPE on the steel sphere was observed (Figure 10d). Such an LDPE layer was not observed for the DCP concentration between 1 and 10 phr. Thus, this layer at 20 phr DCP might be caused by the very brittle polyethylene at high degrees of cross-linking.

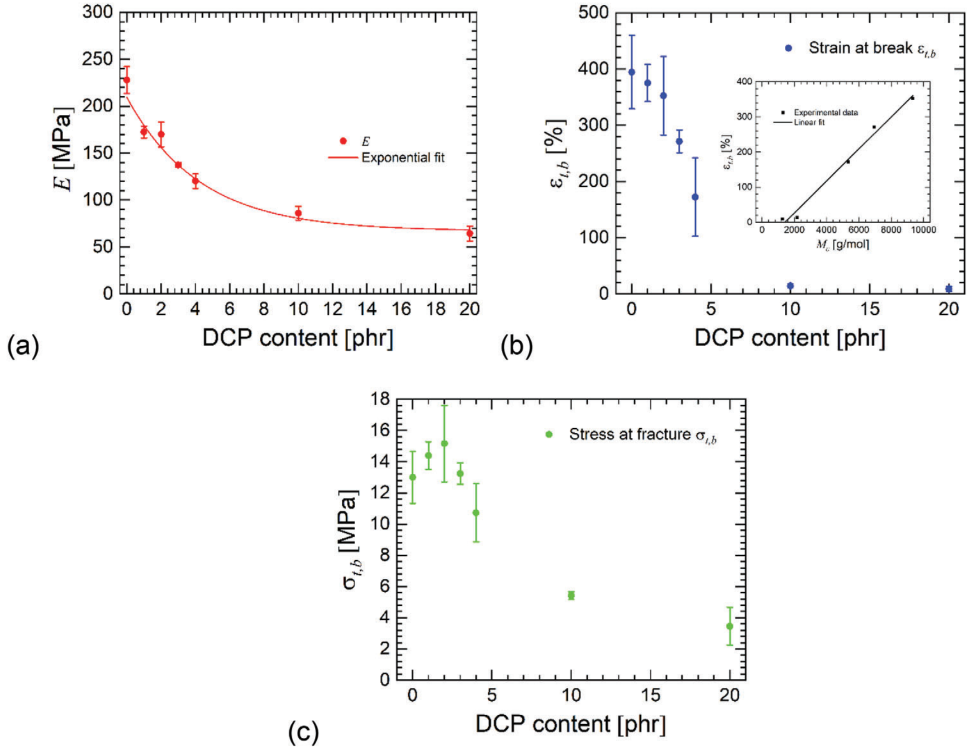

Figure 9. Results of tensile tests at room temperature. a) Modulus E of elasticity, b) strain $\epsilon_{t,b}$ at break and c) stress $\sigma_{t,b}$ at fracture.

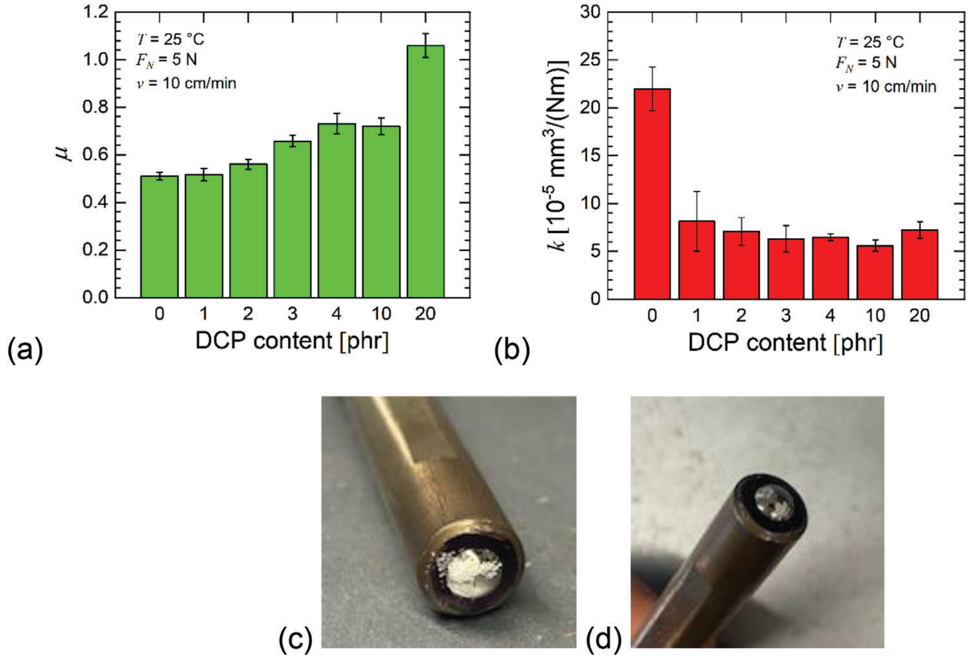

Figure 10. a) Coefficient of friction μ and b) wear rate k as a function of dicumyl peroxide (DCP) concentration. The parameters are $T = 25\,^{\circ}$C, $F_N = 5$ N and $v = 10$ cm min^{-1}. c) Photograph of the steel sphere with the pristine low-density polyethylene (LDPE) (0 phr) after the tribological test. d) Steel sphere with cross-linked LDPE (20 phr) after testing.

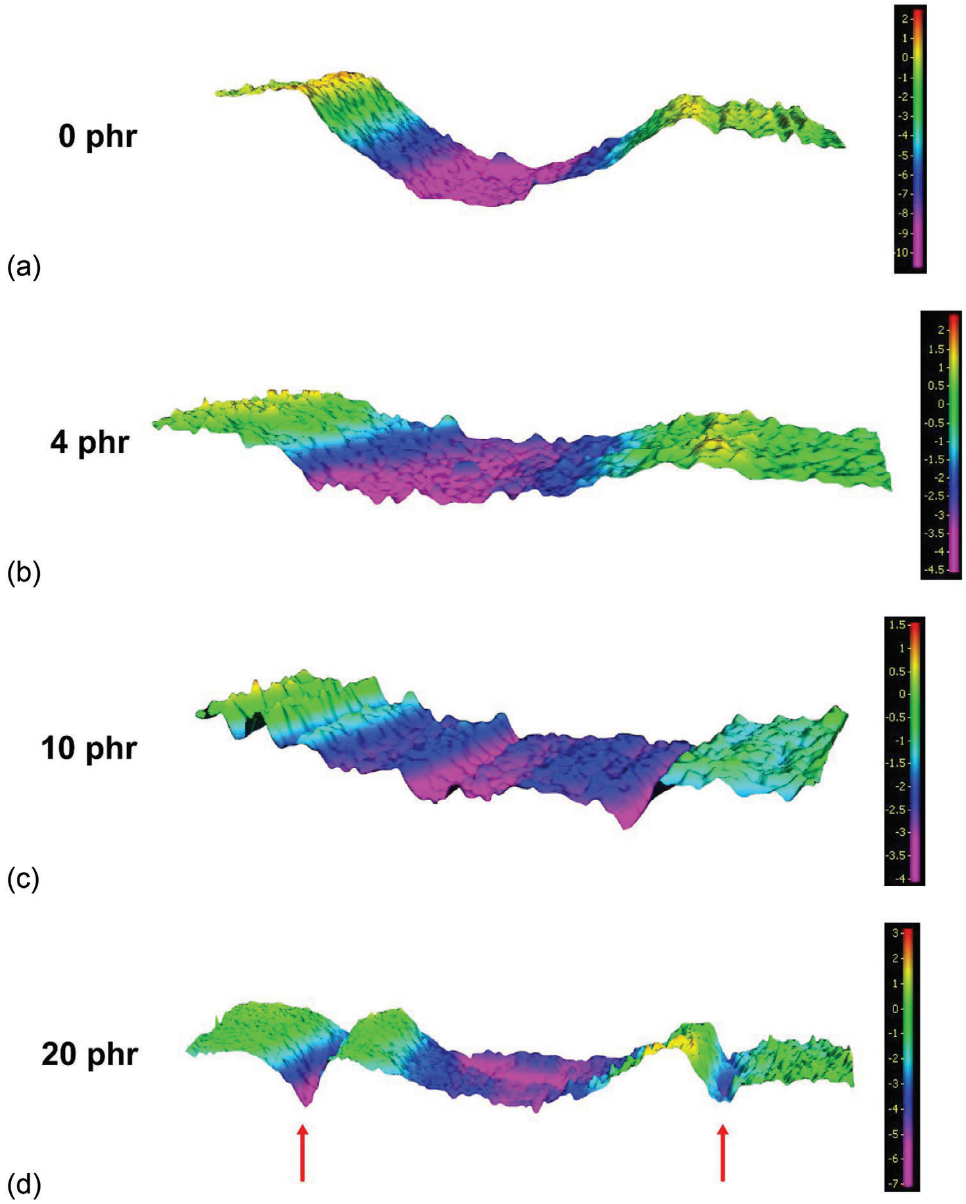

Figure 11. Surface profile in a three-dimensional representation for three dicumyl peroxide (DCP) concentrations a) 0 phr, b) 4 phr, c) 10 phr, and d) 20 phr. The arrows in (c) denote the grooves. The scale bar is given in µm.

The profilometric data in **Figure 11** support these conclusions. Up to a DCP concentration of 10 phr, a monotonic trend revealing the compression of the LDPE sample was observed. At a higher DCP concentration of 20 phr a much stronger mechanical deformation including two outer grooves can be clearly seen.

The results of our tribological tests show that cross-linking is an effective method in order to reduce the specific wear rate of polyethylenes against steel counterparts already at a relatively low degree of cross-linking. The reduction of stiffness caused by the lower degree of crystallinity with increasing DCP concentration tends to increase the contact area between the cross-linked LDPE and the steel sphere.

4. Conclusion

In this study, the influence of DCP concentration on the tribological properties of a cross-linked LDPE was systematically investigated. The focus of this study was the investigation of the effect of high DCP concentrations. In particular, the viscoelastic and tribological properties were correlated. Our data clearly reveal that cross-linking expectedly strongly affects the degree of crystallinity and in this manner the mechanical and tribological properties. In particular, the degree of crystallinity decreases linearly with the degree of cross-linking. In tensile tests under uniaxial loading, the modulus of elasticity and the strain at break decrease with increasing degree of cross-linking. The rheological experiments convincingly show the formation of a network caused by covalent cross-links. Cross-linking efficiently reduces wear of LDPE already at a low DCP concentration, whereas the coefficient of friction significantly increases at a high DCP concentration. This effect can be explained by the increase of contact area at a high DCP concentration (low elastic modulus) and the abrasive wear during the tribological experiments as revealed by our surface analysis. Consequently, large DCP concentrations do not lead to beneficial properties for applications. The study has revealed that the DCP concentration and thus the cross-linking of a common commercial LDPE can be increased up to 10 phr to improve wear resistance. Further increasing the DCP concentration up to 20 phr results in inacceptable embrittlement and reduced wear resistance. This shows that chemical cross-linking of LDPE can improve wear resistance, but to the price of decreased crystallinity and thus decreased stiffness and diminishing strain to break.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

cross-linking, low-density polyethylene, peroxide, rheological properties, tribological properties

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