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Thermal Effects on the Lifetime of Functionalized Nitrile Butadiene Rubber

Zusammenfassung:

Stetige Anforderungen an die Kosteneffizienz und den Umweltschutz treiben die Entwicklung schmierstofffreier Alternativen zum Verschleißschutz elastomerer Bauteile voran. Die Funktionalisierung von Elastomeroberflächen durch die Abscheidung amorpher diamantartiger Kohlenstoffschichten (engl. *diamond-like carbon, DLC*) erweist sich als eine vielversprechende Lösung. Das Reib- und Verschleißverhalten ist abhängig von den Substrateigenschaften und den vorherrschenden Umgebungsbedingungen.

Tribologisch beanspruchte Elastomere finden Anwendung unter erhöhter Temperatur. Die Temperaturerhöhung verändert eine Reihe physikalischer Eigenschaften des gummielastischen Werkstoffes und der DLC Schicht. In dieser Arbeit untersuchen wir den Einfluss der Temperatur auf die Lebensdauer anhand DLC beschichteter Nitrilkautschuke (NBR). Es werden grundlegende mechanische Eigenschaften des Substrates und der Schicht aufgezeigt und anschließend Lebensdaueruntersuchungen durchgeführt. Weiterführend Untersuchungen der nominellen und realen Kontaktfläche werden mit einbezogen.

Abstract:

Lubricants are commonly utilized to reduce the wear of rubber components. The high demand for cost-effective and sustainable alternatives drives the development of alternatives solutions. Functionalizing rubber surfaces by deposition of amorphous diamond-like carbon (DLC) tends to be a promising approach. The friction and wear behavior depends on the substrate properties and the environmental conditions.

Rubber components being applied in tribological set-ups are often exposed to high temperatures. The change in temperature affects the physical properties of the rubbery material and the DLC coating. In this work, we investigate the thermal effects on the durability of DLC coated rubber plates. Nitrile butadiene rubber (NBR) is used as substrate material. The mechanical properties of the substrate and the DLC coating are examined in the shed of elevated temperatures. Subsequently, durability studies are performed. The nominal and real contact area are subject of studies.

1 Introduction

Diamond-like carbon (DLC) is a form of hydrogenated amorphous carbon (a-C:H) with a high fraction of metastable sp³ carbon bonding [1, 2]. Recent studies unveil that DLC films are particularly qualified for components exhibiting high friction due to adhesion, such as elastomers [3-5]. Previous works prove a promising suitability of DLC coatings deposited on rubber. The very good adhesion strength and performance under dynamic test development conditions drives the and research on this topic [6]. The friction and wear performance of DLC coatings on rubber, as applied in this work, are influenced by the film composition as well as the test conditions, test environment, temperature and counterface material [2]. Depending on its glass transition temperature, rubber components are used in a wide temperature range [7]. Thus, high attention is given to tribological applications of DLC coated rubber that are conducted under different thermal conditions.

The following work is about the tribological performance of DLC coated NBR at elevated temperatures. First, substrate properties as well as specific coating properties have been taken into account. Long-term friction tests at several temperatures were performed to evaluate the durability of DLC coated rubber under different environmental conditions. The examination of the nominal and real contact enables further insight into the characteristic film behavior.

2 Experimental environment

2.1 Substrate and coating characterization

The research is based on NBR compounds with different sulfur content (1.5, 3, 6 and 9 phr). The ascending sulfur content during vulcanization leads to higher crosslink density

and, therefore, to different mechanical properties [6]. The viscoelastic substrate behavior was characterized by means of dynamic-mechanical analysis (Netzsch-Gabo Eplexor 2000N). Each measurement was performed at a frequency of 10 Hz in tensile mode. The temperature ranged from -60 to 140 °C. The strain was set between 0.5 to 1.5 % above glass transition temperature. The specimen size was 10 x 35 mm².

The Shore A hardness was quantified according to DIN ISO 7619.

The DLC coating was deposited by means of plasma-enhanced chemical vapor deposition (PECVD). The rubber specimens were coated along with silicon substrates. The latter were used to determine the coating thickness and hardness. Nanoindentations were carried out with a Berkovich-Indenter (Universal Material Tester UMT1, Bruker, USA). Ten measurement points with a maximum force of 0.5 mN were examined. 50 μ m was chosen as distance between each measurement point.

2.2 Friction test

The long-term friction tests were performed with the Universal Material Tester UMT3 by CETR. Rubber samples were adhered to steel sample holders and tempered with the integrated heating element. The ball-on-disc configuration was chosen as tribological setup. The nominal contact area was investigated replacing the 100Cr6 counterpart by a borosilicate ball.

2.3 Digital image processing

The evaluation of the nominal contact area was introduced extensively in [8].



Figure 1: (a) Set-up and (b) – (c) exemplary evaluation of the real contact at RT (0.1 MPa) for 9 phr sample.

For the static real contact area we employed a similar approach, i.e. a Convolutional Neural Network [9,10] with a U-Net architecture [11]. Different from [8] we used the default implementation as provided by the fastai library [12]. As encoder we used a pre-trained ResNet18 [13]. A schematic of the U-Net architecture is provided in figure 2. The network was first trained on 32 images and then evaluated on the remaining 159 images by

visually confirming the correctness of the results. In this work, we define the real contact area as it can be detected optically.



Figure 2: Illustration of a Convolutional Neural Network with U-Net architecture.

3 Results and discussion

3.1 Substrate Properties

Figure 3a depicts the complex modulus of the four substrates in dependence on the sulfur content and temperature. Rubber samples with higher sulfur content exhibit a higher complex modulus (16.3 MPa for 1.5 phr to 37.7 MPa for 9 phr). The modulus decreases with higher temperatures. Likewise, the Shore A hardness climbs to higher values from 69.9 to 85.2 ShA from the least-crosslinked to the highly crosslinked sample at room temperature [6]. Elevating the temperature to 80 °C causes a drop in the hardness for all rubber samples.



Figure 3: (a) Complex modulus in dependence on sulfur content and temperature and (b) Shore A hardness in dependence on sulfur content and temperature.

3.2 Coating properties

The coating properties and the interaction between the temperature and the coating hardness has been investigated for two series of tests. On the one hand, the nanohardness was measured depending on the annealing time at 80 °C. The next step

was to analyze the hardness as a function of the annealing temperature.

As shown in Figure 4a, there is no significant change in the nanohardness over the course of 24 hours annealing time for the samples tempered at 80 °C. The changes of all measured values lie within the standard deviations and measurement accuracy of the test method (7.3 ± 0.85 GPa to 8.25 ± 1.39 after 24 hours). The secondly investigated coating hardnesses for temperatures up to 450 °C are illustrated in Figure 4b. At an annealing time of one hour and temperature up to 350 °C, the nanohardness remains in the range of the coating as it was deposited (7.92 ± 1.33 GPa). At 450 °C a clear decline from 8.2 (350 °C) to 2.05 GPa (450 °C) could be detected.



Figure 4: Coating hardness in dependence on (a) annealing time and (b) annealing temperature.

Thus we can conclude that the coating property, defined by the nanohardness, is stable over the temperature range rubber components are applied (< 150 °C [14]).

3.3 Nominal and real contact area

Recent studies revealed a correlation between the nominal contact area and the substrate hardness [6]. It is assumed that a higher nominal contact area leads to a higher surface pressure and consequently extends the coating durability. In this study, we append the nominal contact area for DLC coated NBR at elevated temperature (Figure 5). The nominal contact area is outlined for short-time tribotests. We choose 300 laps as point of interest, since we expect at this point a steady state with comparatively low influence of wear and debris formation [6]. At room temperature, the nominal contact area is considerably higher for less hard substrate materials (A_{1.5phr,RT,DLC} = 4.72 mm²) than the hard material (A_{9phr,RT,DLC} = 2.7 mm²).

Tempering the substrate to 80 °C leads to higher nominal contact areas for all types of substrates. The nominal contact area increases by 70% to $A_{1.5phr,80^{\circ}C,DLC} = 6.73 \text{ mm}^2$ for the softest material, whereas the area climbs by 73 % to $A_{9phr,80^{\circ}C,DLC} = 3.69 \text{ mm}^2$ for the hardest substrate.



Figure 5: Nominal contact area of DLC coated substrates at room temperature and at elevated substrate temperature.

Figure 6 illustrates the real contact area of different DLC coated substrates at room temperature and elevated temperature of 80 °C. The evaluation method was introduced in 2.3. For all investigations, a steady increase of the real contact area can be detected with higher surface pressure. Comparing the real contact area at room temperature, a significant difference can be deduced between the softer substrates (1.5 and 3 phr) and the harder substrates (3 and 9 phr). DLC coatings deposited on soft substrates tend to exhibit higher values of the real contact area than harder substrates. The differences are more clear at low surface pressures up to 0.4 MPa. At 0.33 MPa, the real contact area decreases from 9.4 % for the 3 phr coated and 8.9 % for the 1.5 phr coated down to 5.8 %for the harder 6 phr and 9 phr substrates, respectively.

Raising the substrate temperature to 80 °C and, therefore, softening the rubber material increases the real contact area for all types of substrates. The overall increase growth is more clear for the harder substrates. Taking the values of 0.33 MPa into account, the real area increases by 1.1 % (1.5 phr), 0.64 % (3 phr), 3.88 % (6 phr) and 3.15 % (9 phr).



Figure 6: Real contact area of (a) 1.5 phr, (b) 3 phr, (c) 6 phr and (d) 9 phr substrates at room temperature and elevated substrate temperature.

It should be noted that crack formation could be detected for the DLC coated 1.5 and 3 phr substrates from 0.4 MPa.

3.4 Tribological tests and durability studies

Long-term friction tests feature a characteristic trend of the coefficient of friction. As demonstrated in Figure 7, the CoF can be split into four major sections. The running-in stage is characterized by a decrease of the CoF. In the second and third stage, here called minimum and increase, the CoF reaches a steady state. Those two stages last

longest with a constantly low CoF. Although crack formation can be identified, no severe damage or delamination is apparent (Figure 8a-c).

Coating delamination and failure is allocated to the following fourth stage. The disclosed uncoated rubber surface leads to an increase in the CoF, as shown in Figure 8d. Stage four is followed by a sharp increase of the CoF. Here, the rubber surfaces is largely exposed and the DLC coating loses its function.



Figure 7: Exemplary trend of CoF during long-term friction test for DLC coated rubber (3 phr at 60 °C).





Figure 8: Surface depiction at different stages for DLC coated 3 phr at 60 °C: (a) Running-in; (b) Minimum; (c) CoF increase; (d) significant wear and delamination.

The aforementioned steady states in stage two and three exhibit an extreme low CoF with a little wear. First delamination and severe wear can be detected in the transition between stage three and four. Although large areas of the rubber surface is still covered by the friction-reducing DLC coating, we choose the transition between stage three to four as the critical point. The values are summarized in Figure 9. Since the evaluation method was not feasible for the samples at room temperature, we replaced the room temperature by a test with 40 °C.

At 40 °C substrate temperature, a clear trend of the number of laps until failure can be seen. The number of laps until failure decreases the higher the hardness of the substrate material becomes. For the DLC coated 1.5 phr sample, the first major delamination can be found after 1.86 x 105 laps, whereas for the DLC coated 9 phr samples the wear limit is detectable after 0.72 x 105 laps. Increasing the substrate temperature from 40 to 60 °C leads to a slightly increase in the coating durability for all substrates unless the 1.5 phr specimen. The changes are as follow: -8 % (1.5 phr), 7 % (3 phr), 28 % (6 phr) and 14 % (9 phr).

A noticeably improve in the coating durability can be found after raising the temperature from 60 °C to 80 °C: 800 % (1.5 phr), 861 % (3 phr), 553 % (6 phr) and 42 % (9 phr).



Figure 9: Durability of DLC coated NBR depending on type of substrate and substrate temperature.

Although each experiment was conducted once, a notable wear resistance could be determined in elevating the substrate temperature.

4 Conclusion

This work comprises the influence of the temperature on the tribological behavior of DLC coated NBR. We studied the substrate properties for a series of differently crosslinked rubber and found, that the substrate properties change in dependence on the temperature. The modulus as well as the hardness can be reduced by elevating the temperature. Further investigations on the DLC coating reveal, that the applied DLC components coating is stable in the range rubber are typically used. Long-term friction tests were conducted after implementing an evaluation method and determining the wear limit of the DLC coating. The wear limit was extended from 1.86×10^5 to 11.88×10^5 for the 1.5 phr (increase by 638 %) and 0.72 x 10^5 to 1.2×10^5 (increase by 66 %), comparing the substrate temperature from 40 to 80 °C.

Investigations on the static real and nominal contact area provide an insight into the load distribution the coating is exposed to. We found, that the nominal and real contact area

depend on the substrate hardness and, thus, the temperature. It is assumed, that an enlarged contact area is beneficial for the coating durability. Further studies are pending in order to prove this theory.

5 Nomenclature

a-C:H	Amorphous hydrogenated carbon
CoF	Coefficient of friction
DLC	Diamond-like carbon
NBR	Acrylonitrile butadiene rubber
phr	Parts per hundred rubber

6 References

1. Robertson, J.: Diamond-like amorphous carbon. Materials Science and Engineering: R: Reports (2002). https://doi.org/10.1016/S0927-796X(02)00005-0

2. Donnet, C., Erdemir, A.: Tribology of Diamond-Like Carbon Films. Springer US, Boston, MA (2008)

3. Adam, A., Paulkowski, D., Mayer, B.: Friction and Deformation Behavior of Elastomers. MSA (2019). https://doi.org/10.4236/msa.2019.108038

4. Martinez-Martinez, D., Schenkel, M., Pei, Y.T., Sánchez-López, J.C., Hosson, J.T.M. de: Microstructure and chemical bonding of DLC films deposited on ACM rubber by PACVD. Surface and Coatings Technology (2011). https://doi.org/10.1016/j.surfcoat.2011.02.067

5. Pei, Y.T., Eivani, A.R., Zaharia, T., Kazantzis, A.V., van de Sanden, M.C.M., Hosson, J.T.M. de: High throughput deposition of hydrogenated amorphous carbon coatings on rubber with expanding thermal plasma. Surface and Coatings Technology (2014). https://doi.org/10.1016/j.surfcoat.2014.02.043

6. Bayrak, S., Paulkowski, D., Stöckelhuber, K.W., Staar, B., Mayer, B.: A Comprehensive Study about the Role of Crosslink Density on the Tribological Behavior of DLC Coated Rubber. Materials (Basel, Switzerland) (2020). https://doi.org/10.3390/ma13235460

7. Röthemeyer, F., Sommer, F.: Kautschuk-Technologie. Werkstoffe - Verarbeitung - Produkte, 3rd edn. Carl Hanser Verlag, München (2013)

8. Staar, B., Bayrak, S., Paulkowski, D., Freitag, M.: A U-Net Based Approach for Automating Tribological Experiments. Sensors (Basel, Switzerland) (2020). https://doi.org/10.3390/s20226703

9. Fukushima, K., & Wake, N. (1991). Handwritten alphanumeric character recognition by the neocognitron. IEEE transactions on Neural Networks, 2(3), 355-365.

10. LeCun, Y., Boser, B. E., Denker, J. S., Henderson, D., Howard, R. E., Hubbard, W. E., & Jackel, L. D. (1990). Handwritten digit recognition with a back-propagation network. In Advances in neural information processing systems (pp. 396-404).

11. Ronneberger, O.; Fischer, P.; Brox, T. U-net: Convolutional networks for biomedical image segmentation. In Proceedings of the Medical Image Computing and Computer-Assisted Intervention (MICCAI 2015), Munich, Germany, 5–9 October 2015; pp. 234–241.

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12. Howard, J.; Gugger, S. Fastai: A Layered API for deep learning. Information 2020, 11, 108, doi:10.3390/info11020108.

13. He, K.; Zhang, X.; Ren, S.; Sun, J. Deep Residual Learning for Image Recognition. In Proceedings of the IEEE Conference on Computer Vision and Pattern Recognition (CVPR 2016), Las Vegas, NV, USA, 27–30 June 2016; pp. 770–778.

14. Krumeich, P., Kmitta, S., Nagdi, K. (eds.): Polymere Dichtungswerkstoffe. Mit 148 Bildern und 56 Tabellen, 1st edn. Resch-Reihe, vol. 3. Resch, Gräfelfing/München (1988).

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