Effect of fullerene C\textsubscript{60} thermal and tribomechanical loading on Raman signals

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\textbf{ARTICLE INFO}

\textbf{Keywords:}
Fullerene C\textsubscript{60}
Raman spectroscopy
Sliding
Laser irradiation

\textbf{ABSTRACT}

Fullerene C\textsubscript{60} powder was loaded by 1 N normal force and exposed to sliding under different frequencies for 15 min. It is shown that the velocity of the sliding movement determines the stability of the fullerene C\textsubscript{60} powder. At slow velocity of movement with a frequency of 1 Hz under 1 N normal force, the fullerene C\textsubscript{60} structure remains undamaged after 15 min sliding. On the contrary, high sliding velocities of 10 Hz and 50 Hz affected fragmentation of the fullerene C\textsubscript{60}, which resulted in a reduction of the coefficient of friction (COF). During sliding with 1 Hz, the friction reached the highest level with an average COF of 0.59 ± 0.03. The faster relative motion under 1 N normal force gave a lower average COF with 0.39 ± 0.03. The initial fullerene C\textsubscript{60} powder formed a thick compressed layer in the tribomechanical loaded zone. As proven by Raman spectroscopy, operating the tribomechanical sliding test at 50 Hz stimulated the re-attraction of fresh C\textsubscript{60} fullerene island onto the fragmented layer from outside of the loaded powder regions. The COF was increasing again up to 0.44 ± 0.04 for 1 N normal force and 50 Hz frequency. The fragmentation and decomposition of fullerene C\textsubscript{60} with increasing sliding velocity is attributed to thermal heating up during fast relative movement. Raman spectra of the tribomechanical loaded fullerene C\textsubscript{60} are compared with Raman spectra from slowly heated up C\textsubscript{60} in air and with Raman spectra of laser irradiated fullerene C\textsubscript{60}.

1. Introduction

Fullerene C\textsubscript{60} win over importance not only due to impressive structural features, but due to the manifold potential applications, like fullerene-based sensors for diverse applications as strain/gas sensors, electrochemical sensors, and optical sensors as well detectors for gases, volatile organic compounds, metal ions, anions, and biomolecules [1]. Due to the extraordinary mechanical properties, fullerene C\textsubscript{60} is used as reinforcement in soft materials [2]. According calculations of Dastjerdi and Akgoz [2,3], the implementation of fullerene structures as reinforcements in composites enhances the strength of the structure significantly more than graphene sheets. Fullerene C\textsubscript{60} can be considered as a promising and cheap organic n-type semiconductor with low activation energy of 0.1–0.3 eV [3]. The conductivity within the material is caused by intrinsic oxygen-related defects [4,5]. Fullerene C\textsubscript{60} is successfully applied as starting material for novel carbon nanocomposite coating (CNC) generation. Khadem et al. [6] applied accelerated buckminsterfullerene C\textsubscript{60} ion-beam bombardment of Ti-substrates for CNCs consisting of graphite nanocrystals enclosed in an amorphous diamond-like matrix. CNCs are formed at relatively high substrate temperatures (300–400 °C) and C\textsubscript{60} ion energies of a few keV [7,8]. In the biomedical field a multitude of established or potential applications opens up for fullerenes. Due to their zero-dimensionality, efficient drug loading and low side effects, fullerene were also found to be suitable candidates for drug delivery [9]. Heredia et al. [10] explain mechanisms for antimicrobial effects of fullerene C\textsubscript{60} derivates. They tested by photodynamic inactivation experiments that cationic fullerenes are highly effective photosensitizers with applications as broad-spectrum antimicrobial agents.

Because of the symmetry of the C\textsubscript{60} molecule (I\textsubscript{h} point group), its 176 vibration modes can be reduced to 46 distinct modes according to the following symmetries: C = 2A\textsubscript{g} + 3F\textsubscript{1g} + 4F\textsubscript{2g} + 6G\textsubscript{g} + 8H\textsubscript{g} + A\textsubscript{u} + 4F\textsubscript{1u} + 5F\textsubscript{2u} + 6G\textsubscript{u} + 7H\textsubscript{u}. Only 10 (2A\textsubscript{g} and 8H\textsubscript{g}) of these modes are Raman active and four (F\textsubscript{1u}) are infrared active. The left over 32 modes are opticaly silent [11]. Three Raman modes, the H\textsubscript{g}(7), the A\textsubscript{g}(2), and the H\textsubscript{g}(8) mode, are surface modes and related to pentagon shear, pentagon
pinch, and hexagon shear modes [12]. In comparison to the experimental results, several theoretical investigations have been published about the calculation of Raman active modes in C₆₀ [12–14].

Multitude of investigations were performed about the decomposition, fragmentation and graphitization of fullerene C₆₀ due to thermal exposure, irradiation processes and exposure to air, metallic surfaces or different particles and nanomaterials [15–27]. Bulgakov et al. [28] report about the stability of hydrothermally and ultrasonically treated fullerene C₆₀. They describe a good stability with only slight changes in the electronic (spin) properties, but an agglomeration. In an early work by Cataldo et al. [29] aggregation of C₆₀ was observed also after treatment of C₆₀ with gamma rays. Their results were supported by Raman and FT-IR spectroscopy. Based on spectroscopic investigations, they describe that a partial oligomerization occurred due to impact of gammy radiation of a dose of 2.6 MGy. Kim et al. [30] successfully hydrothermally treated C₆₀ for receiving ferromagnetic properties at room temperature. They confirmed that defects such as carbon vacancies [31,32] and adatoms of light elements like C, H, N, and O [33–36] are the reasons for manifestation of magnetism in carbon materials. Photo- transformation of bulk C₆₀ in air and laser or electrons beam treatment of C₆₀ films affected changes in the Raman finger print of C₆₀, measurable magnetic features and promoted cluster formation [33]. Defects, clustering, agglomeration and polymerization influence not only magnetic behaviour, but a lot of a fullerene properties. Density functional theory (DFT) studies published by Sabirov et al. [37] have shown that an exaltation of polarizability is typical for dimers of fullerenes. Sun and Reed favour a C₆₀ dimer's co-crystallization by calixarene addition in strictly linear, separated columns [38]. They reasoned that the action of heat and pressure can affect strictly linear nanorods of a [2 + 2] addition polymer (C₆₀)_a and that the calixarenes would prevent crosslinking. Fullerenes have the ability of adsorption. Tukhbatullin et al. [39] describe that the addition of C₆₀ and C₇₀ fullerenes to Tb₂(SO₄)₃·8 H₂O led to a decrease of the photo- and triboluminescence band intensities of Tb³⁺ ion. They assume that there is a radiationless energy transfer from the excited Tb³⁺ ion to the C₆₀ molecule which would bring the fullerene in some kind of an excited state.

The compression behaviour of fullerene C₇₂₀ was investigated by molecular dynamic simulations [40]. The entire compression process of the giant buckyball could be divided into four phases according (I) buckling, (II) post-buckling, (III) densification, and (IV) inverted-cap-forming phase. Pizzagalli [41] state that the mechanical properties of the unique C₆₀ molecule remain poorly known. He published in 2022 density functional theory molecular dynamics calculations of pure compression of C₆₀ at finite temperature, within a large strain range. At engineering strains up to 0.75 ± 0.02, after a 30–32 nN force plateau, stochastic and reversible carbon bond breakings were described by Pizzagalli. For strains larger than an engineering strain of 0.75 ± 0.02, irreversible deformation of the C₆₀ molecule followed.

A chemical change of the endofullerene CH₄@C₆₀ can occur during compression. Sabirov et al. [42] studied by the PBE/3 method that its compression in the direction of opposites hexagons or pentagons should lead to new endohedral covalent derivates. Based on these results, the research group suggests a new technological path for synthesis of endohedrally functionalized fullerene derivatives.

Very few investigations, however, have been published about the effect of tribomechanical loading on the stability of the fullerene C₆₀ molecule structure. Tribomechanical loading includes compression and real contact between the fullerene C₆₀ molecules at the same time. It results in friction as indicated by the coefficient of friction. Due to friction, the mechanical loading is transferred into heat energy. Under ongoing relative movement, the heating up of the contact zones occurs while the pressure endures. If a rolling of the C₆₀ buckyballs occurs during the relative motion, extremely low coefficients of friction can be reached. Such rolling of C₆₀ molecular cages was reported for normal loads in the mN or even nN range only [43,44]. Nakagawa et al. [44] applied a force of 14 nN with an atomic force microscope and became a coefficient of friction of 0.012 with in a small sliding distance below 1 μm. They reported island formation of the C₆₀ film. During their tests, they remained in a single island with the AFM tip. At extremely small load of 0.024 nN, Okita et al. [45] measured the frictional forces of C₆₀ films by scanning force microscopy in dry Argon gas and under 20 % relative humidity RH. They explained that the decrease in frictional force at 20 % RH comes from the lower stiffness of the tip-sample contact, indicating the mobility of C₆₀ molecules, such as easier rolling and/or translation due to water adsorption. Essentially higher normal forces in the Newton range effect a high friction between the fullerene molecules with COFs between 0.4 and 1.0 [46,47]. There is no rolling of the buckyballs but sliding interaction between the C₆₀ molecules. Subsequently, friction during sliding of the carbon molecules against each other occurs. In the present study, a low normal force of 1 N was chosen for loading commercially available fullerene C₆₀ a certain time. The importance of taking the velocity of periodical movement into consideration is proven by Raman spectroscopic investigations of the intermediate medium C₆₀ and the transfer layer after the tribomechanical loading experiments.

2. Materials and methods

2.1. Fullerene C₆₀

The fullerene C₆₀ was purchased from Sigma-Aldrich® (company Merck Darmstadt, Germany) with a purity of 99.9% (article no. 99685-96-8). The fullerenes were investigated in the “as-received” condition as well as after heat treatment in air at 80 °C or 160 °C for 1 h, after tribomechanical loading and different laser irradiations (Table 1). For heat treatment a mass of 250 mg fullerenes were encapsulated in a glass container and positioned in a circulating air oven. The oven type enables a low temperature fluctuation of ±3 °C only.

2.2. FT-IR spectroscopy

For the 80 °C and 160 °C heat treated fullerene C₆₀, infrared spectra were taken in a frequency range of 400–4000 cm⁻¹ in transmittance mode with a spectroscope Jasco FT-IR-6100. KBr pellets of 2 mm in diameter were produced with 10 μg fullerene C₆₀. An agate mortar and pestle are used to mix the fullerene C₆₀ powder with the KBr powder. A mini-press was available to form the 2 mm pellets. Pressure was applied by hand.

2.3. Raman spectroscopy

Raman spectra were acquired at 532 nm wavelength with a Nd:YAG laser of a Renishaw inVia QTTS394 equipment (Renishaw GmbH, Deutschland). It gives more information of the carbon bulk properties instead of just the topmost 10–15 nm reached by UV radiation. The measurement positions were focused at a magnification of 50× in the optical microscope Leica DM4 B (Leica Microsystems GmbH, Germany). The spectral resolution was about 1 cm⁻¹. Raman spectra were recorded by varying acquisition times up to 120 s and 10 accumulations.

Table 1

<table>
<thead>
<tr>
<th>Condition</th>
<th>FT-IR Spectra</th>
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<tbody>
<tr>
<td>C₆₀ “as received” condition</td>
<td></td>
</tr>
<tr>
<td>C₆₀ after 1 h at 80 °C in air</td>
<td></td>
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<tr>
<td>C₆₀ after 1 h at 160 °C in air</td>
<td></td>
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<tr>
<td>C₆₀ irradiated with different laser power (532 nm; Nd-YAG)</td>
<td></td>
</tr>
<tr>
<td>C₆₀ after 15 min at 1 N force and 1 Hz sliding</td>
<td></td>
</tr>
<tr>
<td>C₆₀ after 15 min at 1 N force and 10 Hz sliding</td>
<td></td>
</tr>
<tr>
<td>C₆₀ after 15 min at 1 N force and 50 Hz sliding</td>
<td></td>
</tr>
</tbody>
</table>
2.4. Laser irradiation

For laser irradiations, the laser beam of the Raman spectrometer Renishaw inVia QTT394 equipment (Renishaw GmbH, Deutschland) were used. It is known that carbon allotropes are very sensitive against laser light impact. Different laser pulse length, wave lengths and energy results in many fold structural changes. Irradiation with a green laser of different power finally effects amorphization and graphitisation. Sensitivity against laser irradiation is investigated by stepwise increasing the laser power. 0.1%, 1%, 10%, 50% and 100% laser power of a 45 mW laser (532 nm wavelength) were applied to the “as-received” fullerenes and after 80 °C or 160 °C heat treatment. The structural changes of the fullerenes were recorded in-situ in the correlated Raman signal output.

2.5. Mechanical loading of fullerene C₆₀

In order to mechanical stress the fullerenes, the translatory oscillation apparatus of the company Optimol Instruments GmbH, Munich (Germany) in a ball-on-disk configuration was used. In the present study, a normal force of 1 N were applied on a ZrO₂ ball. The ball moved against a medical grade zirconia ceramic disk with 1 Hz, 10 Hz or 50 Hz, while the sliding distance was 1000 μm for all tests. Subsequently, the sliding speeds of the zirconia ball were 1 mm s⁻¹ for 1 Hz frequency, 10 mm s⁻¹ for 10 Hz frequency and 50 mm s⁻¹ for 50 Hz frequency. The fullerene C₆₀ powder was added as intermediate medium between the ball and the disk (Fig. 1). All sliding tests were performed in laboratory air (relative humidity: 30%; temperature: 25 °C or 160 °C) for 15 min. The coefficients of friction were recorded during the 15 min of sliding. Following sliding tests, Raman spectroscopy was carried out on the fullerenes and their fullerene driven decomposition products in the sliding trace.

3. Results

3.1. Fullerenes C₆₀ at different laser power

The main Raman vibration modes of fullerene C₆₀ are shown in Fig. 2 for laser power of 0.1%, 0.5% and 1%. There are the pentagonal pinch mode Aₕ(2) at about 1469 cm⁻¹, the Hₕ(7) mode at around 1424 cm⁻¹ and the Hₕ(8) mode at 1541 cm⁻¹. Obviously, with a laser power of 1%, there is a red shift of the Aₕ(2) mode in comparison to the 0.1% and the 0.5% laser power irradiation (Fig. 2).

In addition, especially from the Raman spectra at lower laser power of 0.1% and 0.5%, it is evident that the prominent Aₕ(2) mode is split into several bands. For 0.1% laser power, at least two bands of the Aₕ(2) mode can be clearly identified. They are located at 1462 cm⁻¹ and 1471 cm⁻¹ (Fig. 3, Table 2). In the present study, the band at a position of 1462 cm⁻¹ is named Aₕ(2)₁ and the peak with a position at 1471 cm⁻¹ is assigned to the before mentioned prominent fullerene C₆₀ finger print pentagon pinch mode of C₆₀ monomers.

The aforementioned red shifted Aₕ(2)₁ mode from laser irradiation with 1.0% is a summary of several Raman bands also. Although, the overlapping of the three peaks suggests the impression of a single, red shifted band, it can be deconvoluted into peak positions at 1468 cm⁻¹, 1462 cm⁻¹ and 1457 cm⁻¹ (Table 2). The intensity ratios of the prominent fullerene C₆₀ monomer pinch mode Aₕ(2)₁ peak at around 1469 cm⁻¹ to the Aₕ(2)₂ at around 1462 cm⁻¹ or the peak at 1456 cm⁻¹, which is named as Aₕ(2)² in this study, are calculated and summarized in Table 2 as well. The Aₕ(2)₁/Aₕ(2)₂ ratio seems not to be dependent on the laser power. However, the Aₕ(2)₁/Aₕ(2)² ratio increased with increasing laser power of 0.1% to 0.5% from almost zero to 4.4 (Table 2). Further increasing the power of laser irradiation on “as received” fullerene C₆₀ to 5% resulted in new broad Raman bands with peak positions at wavenumbers of 1385.4 cm⁻¹ and 1596.0 cm⁻¹ (Fig. 4, Table 3). The 1596.9 cm⁻¹ Raman peak is due to the stretching mode of sp²-hybrised C-C-
Defective graphene contributes to the Raman spectra at certain laser power.

3.2. Fullerene C₆₀ before and after heat treatment at 80 °C and 160 °C

Also, heating up the fullerenes C₆₀ leads to a changed Ag(2) peak. It is obvious from Table 4 and curves (a) and (b) in Fig. 6 that a temperature exposure of 80 °C for 1 h does not essentially change the Ag(2) band. However, the 1 h temperature exposure at 160 °C effected a change of the single peaks of the Ag(2) family. The intensity of the pentagonal pinch mode of fullerene C₆₀ monomers is reduced in comparison to the intensity of the Ag(2) family after 160 °C temperature exposure in air. In addition to the pentagonal pinch mode of single fullerenes C₆₀ at around 1469 cm⁻¹ according Bethune et al. [13], two more peaks were contributing to the broad band. Again the Ag(2)₁ peak at around 1462 cm⁻¹ can be identified for all three conditions of C₆₀-the “as received” state, after heat treatment at 80 °C and after 1 h heating at 160 °C. However, the Ag(2)₂ peak intensity increased. The Ag(2)/Ag(2)₁ intensity ratio has a value of 2.3 for the “as received” C₆₀ while after heat treatment at 80 °C it is 1.1 and after heat treatment at 160 °C 0.45 only. Additionally, a peak at wavenumber around 1457 cm⁻¹ can be identified after heat treatment of 160 °C for 1 h.

There was no change observable in fullerene C₆₀ structure by using FT-IR spectroscopy. FT-IR spectra of C₆₀ in the “as received” condition from harsh irradiation at 80 °C and 160 °C gave exactly the same curvature and peaks (Fig. 7) with peaks at 1538 cm⁻¹ , 1181 cm⁻¹ and 574 cm⁻¹ as well as 525 cm⁻¹ . The full width at half maximum of Raman peaks is between 5.5 and 9.2 cm⁻¹ (Table 5).

3.3. Fullerene C₆₀ tribomechanical loading

During sliding with a normal force of 1 N and a frequency of 1 Hz an average friction coefficient of 0.59 ± 0.03 (Table 6) was measured. It is essential higher than the coefficient of friction measured for fullerene C₆₀ at intermediate medium at higher frequencies of 10 Hz or 50 Hz. For 10 Hz frequency a COF of 0.39 ± 0.03 were determined. The frequency of 50 Hz resulted in an average friction coefficient of 0.44 ± 0.04
The COF curve progressions at 1 Hz and at 10 Hz are rather similar (Fig. 9a). Following a fast increase of the friction in the running in stage, there is a steady drop to lower values. The COF curves are not smooth and homogeneous, but rise again slowly before they afterward fall again moderately. The friction proceeding seems to be different for 50 Hz. Although the COF curve at 50 Hz is almost superposable to the COF curve at 10 Hz, sudden sharp increases of the COF happen to friction levels around the values at 1 Hz (Fig. 9b).

Table 4
Raman data of fullerene C$_{60}$ before and after heat treatment at 80 °C and 160 °C (0.1% laser power; see Table 2).

<table>
<thead>
<tr>
<th>C$_{60}$ sample</th>
<th>H$_{g}(7)$ position [cm$^{-1}$]</th>
<th>$A_y(2)$ peak w/o polymerization position [cm$^{-1}$]</th>
<th>$A_y(2)^{1}$ peak polymerized dimers position [cm$^{-1}$]</th>
<th>$A_y(2)^{2}$ peak polymerized linear chains position [cm$^{-1}$]</th>
<th>$A_y(2):A_y(2)^{1}$ intensity ratio</th>
<th>$A_y(2):A_y(2)^{2}$ intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$ &quot;as received&quot;</td>
<td>1426.86</td>
<td>1470.99</td>
<td>1462.71</td>
<td>–</td>
<td>2.30</td>
<td>–</td>
</tr>
<tr>
<td>C$_{60}$ after 80 °C</td>
<td>1427.49</td>
<td>1471.18</td>
<td>1461.78</td>
<td>–</td>
<td>1.10</td>
<td>–</td>
</tr>
<tr>
<td>C$_{60}$ after 160 °C</td>
<td>1428.60</td>
<td>1471.16</td>
<td>1462.71</td>
<td>1455.01</td>
<td>0.45</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Fig. 6. Raman spectra from irradiation with 0.1%, of the laser power of fullerene C$_{60}$ in the “as received” condition and after heat treatment at 80 °C and 160 °C.

Table 5
Halfwidth of C$_{60}$ bands from two colloidal systems.

<table>
<thead>
<tr>
<th>Peak position [cm$^{-1}$]</th>
<th>Halfwidth [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$ &quot;as received&quot;</td>
<td>525 9.2</td>
</tr>
<tr>
<td></td>
<td>574 6.0</td>
</tr>
<tr>
<td></td>
<td>1181 7.4</td>
</tr>
<tr>
<td></td>
<td>1428 7.8</td>
</tr>
<tr>
<td>C$_{60}$ after 1 h at 80 °C in air</td>
<td>525 8.3</td>
</tr>
<tr>
<td></td>
<td>574 7.0</td>
</tr>
<tr>
<td></td>
<td>1181 7.4</td>
</tr>
<tr>
<td></td>
<td>1428 8.0</td>
</tr>
<tr>
<td>C$_{60}$ after 1 h at 160 °C in air</td>
<td>525 7.9</td>
</tr>
<tr>
<td></td>
<td>574 5.5</td>
</tr>
<tr>
<td></td>
<td>1181 6.8</td>
</tr>
<tr>
<td></td>
<td>1428 7.2</td>
</tr>
</tbody>
</table>

Table 6
COF$^a$ of fullerene C$_{60}$ covered medical grade zirconia (counter body: zirconia ball; F$_n$: 1 N; stroke 1000 μm).

<table>
<thead>
<tr>
<th>Sliding frequency</th>
<th>COF</th>
<th>COF$_{10min}$</th>
<th>COF$_{15min}$</th>
<th>COF$_{15min}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Hz</td>
<td>0.59 ± 0.03</td>
<td>0.57</td>
<td>0.62</td>
<td>0.57</td>
</tr>
<tr>
<td>10 Hz</td>
<td>0.39 ± 0.03</td>
<td>0.37</td>
<td>0.40</td>
<td>0.37</td>
</tr>
<tr>
<td>50 Hz</td>
<td>0.44 ± 0.04</td>
<td>0.43</td>
<td>0.43</td>
<td>0.45</td>
</tr>
</tbody>
</table>

$^a$ Coefficient of friction.

Fig. 7. FT-IR spectra of fullerene C$_{60}$ “as-received” and after 80 °C and 160 °C heat treatment.
In the case of 1 Hz sliding movement, optical microscopy and Raman spectroscopy (Fig. 10a) confirmed that the fullerene C60 molecules stay undamaged. The peak positions and shapes are equal to the “as-received” condition after 15 min tribomechanical loading with 1 N normal force and 1 Hz sliding frequency. The main intensity peak is shifted slightly from characteristic 1469 cm\(^{-1}\) position to a wavenumber of 1472 cm\(^{-1}\). In addition to this prominent main peak, there are less intense Raman peaks at 1462 cm\(^{-1}\) and 1469 cm\(^{-1}\) (Figs. 10a, 11). Also, there are the H\(_6\)(6) peak at 1572 cm\(^{-1}\) and a Raman signal at 500 cm\(^{-1}\) which belongs to the A\(_5\)(2) pentagonal pinch mode. No other phases were identified after tribomechanical loading with 1 N normal force and after 1 Hz sliding frequency.

![Graph showing friction coefficient vs. time for different frequencies.](image-url)

**Fig. 8.** Average coefficient of friction of fullerene C\(_{60}\) loaded with 1 N normal force at different frequencies.

![Graph showing friction coefficient vs. time for different frequencies.](image-url)

**Fig. 9.** Coefficient of friction of fullerene C\(_{60}\) loaded with 1 N normal force at different frequencies: (a) 1 Hz and 10 Hz; (b) 1 Hz, 10 Hz and 50 Hz.

For a faster sliding movement of 10 Hz, the fullerene C\(_{60}\) feature can’t be identified in the Raman spectrum easily (Fig. 10b), but two separated main peaks are clearly evident. The Raman peak at a wavenumber of 1350 cm\(^{-1}\) point to phase transformation of the fullerene C\(_{60}\) under the impact of the higher frequency. The peak positions were determined by automatic fitting function of the software wire 4.2. The G peak can be found at a wavenumber of 1590 cm\(^{-1}\) and the D peak at 1350 cm\(^{-1}\). By having a closer look at the Raman bands between 1000 cm\(^{-1}\) and 1900 cm\(^{-1}\), it is evident that the band before the G peak is arising by overlapping of several single peaks (Fig. 12, Table 7). Deconvolution of the curve gave peak positions at 1469 cm\(^{-1}\) and 1070 cm\(^{-1}\) in addition to the D peak centre at 1350 cm\(^{-1}\).

The fasts sliding with 50 Hz stimulated the evolution of D peak centred at 1350 cm\(^{-1}\) and a G peak centred at 1598 cm\(^{-1}\) (Figs. 10c, 13, Table 7). The sliding trace showed an inhomogeneous appearance. There were dark grey regions with strip-like arranged grooves (position 1 in Fig. 10c) visible in the light microscope. These greyish regions were decorated by black roundish islands (position 2 in Fig. 10c). The greyish regions gave the impression of a film in the light microscope and the already described Raman fingerprint with peaks centred at 1350 cm\(^{-1}\) and 1598 cm\(^{-1}\). The darker roundish islands were identified as undamaged fullerene C\(_{60}\). For the detailed determination of the topology of the tribomechanical loaded carbon, confocal laser microscopy was applied. It confirmed that the greyish regions are coverings of some 100 nm thickness. Fig. 14 shows the edge of a covering from the tribomechanical loaded zone with C\(_{60}\) as initial intermediate medium and after the loading with 1 N and 50 Hz. It can be seen that the thickness of the cover from formerly fullerene C\(_{60}\) powder amounts to 832 nm at the measurement position. Fig. 15 displays the tribomechanical loaded region. The smeared coverage (position 1 in Fig. 10c) can be recognized again, but in addition an aforementioned undamaged fullerene C\(_{60}\) island is visible (red coloured in Fig. 15, position 2 in Fig. 10c). This fullerene sparkle has a high of 4.5\(\mu\)m. It is about 5–6 times higher in comparison to the compressed carbon coverage.

### 4. Discussion

#### 4.1. FT-IR spectroscopy

C\(_{60}\) shows characteristic IR active vibrational F\(_{1u}\) modes at around 526, 575 and 1183 and 1428 cm\(^{-1}\) [13,18,19]. According Bethune et al. [13], a weak feature at around 1540 cm\(^{-1}\) remains unexplained. Andrievsky et al. [19] noted that halfwidths of the vibrational bands depend on C\(_{60}-C_{60}\) interactions. They investigated two types of fullerene-water colloidal systems: molecular-colloidal C\(_{60}\) solution in water (C\(_{60}\)FWS) and typical monodisperse C\(_{60}\) hydrosol (C\(_{60}\)hH).

Andrievsky et al. report that for the fullerenes from C\(_{60}\)hH, the halfwidths of the vibration bands are 1.2–2.6 times greater than for C\(_{60}\) from C\(_{60}\)FWS and argue that a widening of the main C\(_{60}\) vibration bands is due to the before mentioned C\(_{60}-C_{60}\) interactions. The molecular-colloidal C\(_{60}\) solution C\(_{60}\)FWS consisted of isolated C\(_{60}\) molecules in crystal-like hydrophobic C\(_{60}\) nanoparticles.

As visible from Table 5 and Fig. 7, the FT-IR peak positions of C\(_{60}\) in air remain almost constant. However, broadening of 1181 cm\(^{-1}\) and 1428 cm\(^{-1}\) peaks are reported to be indicative for cross-linking and polymerization by breaking of \(\pi\)-bonds in two neighbouring molecules. In an early work, Pukha et al. [20] report not a broadening of the FWHM, but two peaks, the peak at 1428 cm\(^{-1}\) and the photopolymer peak at 1424 cm\(^{-1}\). They state that these two peaks are very clear markers of polymerization. In their work, an irradiation reduced the C\(_{60}\) peak at 1428 cm\(^{-1}\) while it increased the polymerization peak at 1424 cm\(^{-1}\).
No sign of increased polymerization due to exposure of the received C$_{60}$ fullerenes to temperatures of 80 °C or 160 °C in air can be seen in the present study. However, with a full width at half maximum (FWHM) between 7.2 and 8.0 cm$^{-1}$ for the 1428 cm$^{-1}$ band, the FWHM is in the range polymerized C$_{60}$ in the initial “as received” condition already. Kumar et al. [21] report a FWHM of around 5.5 cm$^{-1}$ for non-ion irradiated C$_{60}$. A polymerization due to ion irradiation by 200 MeV Au ions with around $1 \times 10^{13}$ ions/cm$^2$ gave a FWHM of the 1428 cm$^{-1}$ peak of about 8 cm$^{-1}$, which is in the dimension of the present results. As also mentioned by Pukha et al. [20] and measured by Iwasa in an early work [22], a further increase of temperature leads to de-polymerization, while the polymers convert into monomers again.

Fig. 10. Surface and Raman spectra of fullerene C$_{60}$ loaded medical grade ZrO$_2$ after tribomechanical loading with 1 N normal force and (a) 1 Hz, (b) 10 Hz and (c) 50 Hz. Measurement positions of Raman spectroscopy (532 nm) are marked green. Light microscopy. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
4.2. Raman spectroscopy

4.2.1. Impact of laser irradiation with different power on fullerene C_{60} 

The red shift of the C_{60} A_{g}(2) peak is correlated by Kopova et al. [23] with an alteration of the chemical bonding of the fullerene C_{60}, such as polymerization (interaction of C_{60} which each other and formation of a polymerized C_{60} network) and oxidation (chemical bonding of oxygen with C_{60}). Razanau et al. [24] deposited fullerene C_{60} films coatings of 200 nm from the gas phase by electron beam dispersion (EBD) of fullerite powder. In the Raman spectrum of EBD C_{60} coatings bands characteristic of fullerene monomers, dimers, linear polymer chains and 2D polymer networks were confirmed by Razanau et al.. They describe that the A_{g}(2) pentagonal pinch mode is an excellent indicator of C_{60} polymerization process. There are additional Raman bands, the shift of active modes and the activation of silent modes in polymerized C_{60} due to the covalent bonds between the molecules, which reduce molecular symmetry. Raman spectra of the crystalline polymerized phases allow to distinguish between dimers at frequencies of 1462 cm\(^{-1}\), linear chains at 1457 cm\(^{-1}\), and 1449 cm\(^{-1}\) and 1406 cm\(^{-1}\) for tetragonal and rhombohedral 2D polymer networks [2,24]. Subsequently, in the present study, the peak position at 1462 cm\(^{-1}\) can be correlated to dimers in the polymerized C_{60}. Thermal breakdown of C_{60} dimers can occur at temperature above 177 °C according [25]. Meletov et al. [16] investigated fullerene C_{60} with 2-dimensional rhombohedral polymer structure and

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**Table 7**

<table>
<thead>
<tr>
<th>Tribomechanical loading parameters</th>
<th>A_{g}(2) peak position [cm(^{-1})]</th>
<th>A_{g}(2) peak position [cm(^{-1})]</th>
<th>A_{g}(2) peak polymerized dimers position [cm(^{-1})]</th>
<th>D peak position [cm(^{-1})]</th>
<th>G peak position [cm(^{-1})]</th>
<th>(I_p/I_G) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal force (F_n)</td>
<td>Frequency</td>
<td>Time</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 N; 1 Hz; 15 min</td>
<td>1472</td>
<td>1469</td>
<td>1462</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1 N; 10 Hz; 15 min</td>
<td>(A_g(2)) ensemble</td>
<td>–</td>
<td>–</td>
<td>1350</td>
<td>1600</td>
<td>0.52</td>
</tr>
<tr>
<td>1 N; 50 Hz; 15 min</td>
<td>Position (1)</td>
<td>–</td>
<td>Position (2)</td>
<td>1471</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

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**Fig. 11.** Raman spectrum (532 nm; 0.1% laser power) of fullerene C_{60} loaded medical grade ZrO\(_2\) after tribomechanical loading with 1 N normal force and 1 Hz: 1400 cm\(^{-1}\) to 1500 cm\(^{-1}\). 

**Fig. 12.** Raman spectrum (532 nm; 0.1% laser power) of fullerene C_{60} loaded medical grade ZrO\(_2\) after tribomechanical loading with 1 N normal force and 10 Hz: 1000 cm\(^{-1}\) to 1900 cm\(^{-1}\).
confirm that it remains stable after 0.5 h treatment up to 230 °C.

In an early work of Iwasa [22], polymer reversion to monomers is reported to occur in an endothermic reaction upon heating to 300 °C. They suggest that molecular deformation plays a crucial role in the energetics of C60 polymers. Additional energetic impact can lower the threshold for thermal breakdown in fullerene dimers and polymers and accelerate the dissociation or even fragmentation of fullerenes [17,22,25,26]. Apparently, in the present study, an increased laser power from 0.1% to 1% of the 45 mW Nd-YAG laser does not influence the fraction of fullerene C60 dimers essentially. The intensity and position of the polymerized dimer A1g(2) peak at 1469 cm$^{-1}$ stayed rather similar at 0.1%, 0.5% and 1% laser power with peak centres at 1462.71 cm$^{-1}$, 1462.61 cm$^{-1}$ and 1462.78 cm$^{-1}$ (Fig. 2, Table 2). On the other hand, the polymerized linear chains A2g(2) peak is influenced by the

![Graph showing Raman spectrum](image)

**Fig. 13.** Raman spectrum (532 nm; 0.1% laser power) of fullerene C60 loaded medical grade ZrO2 after tribomechanical loading with 1 N normal force and 50 Hz: 1000 cm$^{-1}$ to 1900 cm$^{-1}$.

![Image showing sliding trace](image)

**Fig. 14.** Sliding trace after tribomechanical loading of C60 with 50 Hz frequency, Laser microscopy.
laser power. At 0.1% laser power, no \( A_2(2)^2 \) signal was evident (Fig. 2, Table 2). Higher laser power of 0.5% and 1% increased the intensity of the linear polymer chains \( A_g(2)^2 \) peak with an \( A_g(2):A_g(2)^2 \) ratio of 2.9 for 0.5% and 4.4 for 1% laser power. There is a minor red shift of the \( A_g(2)^2 \) and the \( H_g(8) \) peak positions with increasing fraction of the linear polymer chains. At the same time, the fullerene \( C_60 \) monomer \( A_g(2) \) pentagon pinch mode decreases in intensity and red shifts from 1470.00 cm\(^{-1}\) for 0.1% laser power to 1470.78 cm\(^{-1}\) for 0.5% laser power and 1468.00 cm\(^{-1}\) for 1.0% laser power (Table 2). The monomer fraction is reduced and more linear polymeric \( C_60 \) chains are generated if laser power is increased from 0.1% to 1%.

If high thermal excitation and/or pressure are acting upon fullerenes, at a certain point fragmentation and an amorphous structure arises [27,48]. Ongoing thermal and energetic exposure results finally in graphitization. At 5% laser power the \( A_g(2) \) modes remains as a prominent feature of the Raman spectra at Fig. 5, Table 3. However, the two specific peaks of defective graphite-like carbon peaks give the Raman spectra a different appearance. The D-peak, which is originated by the breathing mode of defective sp\(^2\)-hybridised aromatic C–C rings, around 1350 cm\(^{-1}\) became evident. Also, the G-band, which is due to the stretching mode of sp\(^2\)-hybridised C–C bonds at about 1580 cm\(^{-1}\) can be seen. At 5% laser power, the D band position is 1385.4 cm\(^{-1}\). The centre of the G-peak is located at 1596.0 cm\(^{-1}\) (Fig. 5, Table 3). 10% laser power gave a D-band at 1375.8 cm\(^{-1}\) and a G-peak at 1593.8 cm\(^{-1}\), while for 50% laser power D-band is located at 1348.4 cm\(^{-1}\), the position of the G-band centres at 1592.6 cm\(^{-1}\). In addition, a band at 2655.7 cm\(^{-1}\) (Fig. 5, Table 3) points to the contribution of defective graphitic after 50% laser power irradiation. At 100% laser power, neither the fullerene \( C_60 \) contribution to the Raman spectrum is visible, nor any defective graphitic signals, but a complete degradation of buckyball structure to graphite-like sp\(^2\)-hybridised configuration with defective graphite peak centred at 1373.5 cm\(^{-1}\) (Fig. 13, Table 3). The intensity ratio of D- and G-peak \( I_D/I_G \) is around 0.8 and seems to be independent on the laser power.

4.2.2. Impact of gentle heat treatment on fullerene \( C_60 \)

Also, a minor and gentle heat treatment can change the polymerization of fullerene \( C_60 \). It is evident from the Raman spectra (Fig. 6). After the exposure of fullerene \( C_60 \) for 1 h at 160 °C, the intensity of the dimer peak at 1461.78 cm\(^{-1}\) is increased essentially, while the intensity of the monomer \( C_60 \) peak at 1471.16 cm\(^{-1}\) suffers (Fig. 6, Table 4). The \( A_g(2)/A_g(2)^2 \) ratio is 0.45 only after 160 °C heat treatment. In comparison to the “as received” condition of fullerene \( C_60 \), the \( A_g(2)/A_g(2)^2 \) ratio is reduced by 5 times. The dimer formation is strongly promoted at 160 °C. In addition, linear chains develop after 1 h at 160 °C, which is evident from the \( A_g(2)^2 \) peak at 1455.01 cm\(^{-1}\). No characteristic peak for linear polymer chain configuration of fullerene \( C_60 \) can be seen after heating to only 80 °C for 1 h or in the “as received” condition.

4.2.3. Impact of normal force and sliding on fullerene \( C_60 \)

During all tribomechanical tests, a normal force of 1 N was acting on a zirconia ball that transferred the load on the fullerene \( C_60 \) agglomerates. As the fullerene \( C_60 \) powder was spread out on a zirconia plate before loaded with the ball, it is clamped during the loading. It receives kinetic energy from the ball movement. The ball did slide across the zirconia plate surface, which had the fullerenes \( C_60 \) on top. The fullerene powder is not distributed as a single \( C_60 \) layer but forms agglomerates which are pressed together to a certain extend due to the normal force.

The buckyballs were loaded (a) by normal force (Fig. 16a), but due to the sliding of the zirconia ball against the surface, (b) horizontal and (c) vertical shearing as well as combinations of (a), (b) and (c) were simulated. If mere elastic contact occurs, an extremely high Hertzian pressure of several hundred MPa would act between two single buckyballs. The kinetic movement of the buckyballs was accompanied by a certain degree of thermal local heating due to the friction along the contact areas (Fig. 17) during the relative movement between zirconia ball and disk as well as between the \( C_60 \) buckyballs. Such a harsh mechanical loading will destroy the fullerene \( C_60 \) after short while.

Obviously, after 15 min sliding of the zirconia ball along the buckyball decorated disk surface with 1 Hz, the buckyball structure of the fullerene \( C_60 \) was sustained very well. The prominent \( A_g(2) \) band is dominating the Raman spectra after 15 min sliding at 1 Hz (Fig. 10a). However, after the mechanical loading with 1 N and 1 Hz, a slight upshift of the \( A_g(2) \) mode to 1472 cm\(^{-1}\) was measured (Fig. 11). The intensity of the Raman peak at 1472 cm\(^{-1}\) is high, in comparison the peaks at 1469 cm\(^{-1}\) and 1462 cm\(^{-1}\). The latter peak can be clearly assigned to fullerene \( C_60 \) dimer configuration, while the 1469 cm\(^{-1}\) centred band is attributed to the monomer \( A_g(2) \).

Sliding and friction also cause an activation of the fullerene \( C_60 \).
which maybe adsorbs substances from the surrounding environment like oxygen or humidity. In the case of water-fullerene C_{60} molecule interaction a blue shift of the A_g(2) and the H_g(7) peaks were reported by Amer [14]. The degree of peak position shift depends on the number of adsorbed water molecules. Amber et al. calculated a maximum shift of some 12–15 wavenumbers for 60 water molecules, while for less adsorbed water the shift is only some wavenumbers. The calculated blue shift of the Raman signals was later confirmed by experimental measurements of C_{60} molecules in water [49].

Another reason for shifts of fullerene C_{60} peak positions to higher wavenumbers is pressure [50]. The frequencies of most fullerene C_{60} Raman modes including the A_g(2) mode increase with increasing pressure. Meletov et al. [50] define a pressure coefficient. They report that the pressure driven shift of the Raman signals can be in the range of minus 0.2 to 9.8 cm\(^{-1}\)/GPa for pristine C_{60} and pressures between 0.2 GPa and 2.4 GPa in example. As stated before, due to the mechanical loading of the buckyballs with 1 N normal force under ongoing sliding with 1 Hz, Hertzian pressure between the fullerene C_{60} molecules reaches an enormous level.

After release of loading, there may remain some residual stresses due to displacement of bonding, which could result in peak shifts. Another reason for the small increase of A_g(2) peak position in wavenumber is imaginable. The 1472 cm\(^{-1}\) centred prominent band is only up shifted very slightly. Because the tests were carried out in laboratory air with an average humidity of 30%, adsorption of water molecules may be another reasonable cause for the observed minor peak shifting. The phenomenon of atom, ion and water molecule adsorption is very well known for activated surfaces in tribo-contact zones with freshly formed unsaturated bonds [43,51–53]. It is commonly supported by the high pressures and under ongoing frictional activation.

By increasing the frequency to 10 Hz, the decomposition of the buckyballs is evident from the Raman spectrum (Fig. 10b). Hereby, the
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ion bombardment is able to transform and destroy the buckyball structure 
out to the formation of defective graphite-like carbon. Also, energetic 
normal forces in the nN range [43,45]. Hereby, a rolling of the bucky 
balls is initiated which is apparently not stimulated in the powder ag 
gromerates in the present work.

Hereby, the friction was favoured in comparison to the not graphite-like 
g60 powder with an average COF of 0.39 ± 0.03 (Figs. 8, 9a), which may be 
attributed to the good properties of graphite and graphite-like carbon as 
solid lubricant in humid environments (RH 30%). At higher frequency of 
50 Hz, the COF curve was mainly at the same level like for the 10 Hz 
sliding at 1 N normal force. However, sudden spontaneous increases of 
the COF were seen at the curve (Fig. 9b). This behaviour gave an average 
COF of 0.44 ± 0.04 for 50 Hz sliding (Fig. 8).

After 15 min under 1 N and 50 Hz sliding with 50 Hz, the C60 
structure of carbon was destroyed (Figs. 10c, 13). As obvious by mi 
roscopy, a compacted layer was formed. On top of the graphite-like 
carbon layer, islands with an essential higher topography were 
observed (Fig. 15). It were identified as fullerene C60 agglomerates by 
Raman spectroscopy (Fig. 10c, position 2). Apparently, a re-attraction of 
C60 onto the consolidated and modified former fullerene C60 layer took 
place. Fresh and undamaged buckyball islands emerged under the 
vibrational stimulation of fast 50 Hz sliding. Due to the vibration under 
high frequencies of 50 Hz, light fullerene C60 particles were shook and 
transported from the non-consolidated edges of the loaded contact zones 
and decorated it freshly. The newly supplied fullerene C60 islands locally 
increased the COF to the level of undamaged C60 for a short time as 
observed.

5. Conclusions

During 1 N loading of a zirconia ball, slow periodic motion with 1 Hz 
for 15 min does not cause the formation of linear oriented C60 polymer 
chains along the sliding trace. Also, 2-dimensional tetrahedral or 
rhombohedral polymer networks were not observed. The minor 
adsorption of molecules on C60 monomers may be responsible for a 
minor blue shift in wavelength of the A2(2) monomer peak Raman 
signal.

Instead, polymeric C60 chains are favoured by a gentle heat treat 
ment at 160 °C for 1 h without mechanical loading. On the same 
occasion, the C60 dimer fraction is reduced, and, it can be concluded that 
the former buckyball dimers re-organized to shape into the linear C60 
polymer chains. After careful laser irradiation with low power, the 
fullerene C60 polymeric chain structure is formed as well.

Increased laser power or high sliding frequencies during loading fast 
destroy the fullerene C60 buckyball structure. As reasons for the degra 
dation of the C60 cage molecules several mechanisms are known, which 
include heat and pressure. Care must be taken in order to optimize the 
tribological loading system in order to prevent or control breakage of 
the fullerene configuration during sliding under high frequencies.

A re-attraction of fresh fullerene C60 particles can be stimulated by 
high frequency movement, if the carbon molecules are not strong fixed 
on the substrate like valid for loosely layed-off powder covers. Due to 
the lightweight cage-like structure and low density of C60 powder, 
agglomerate island could newly be generated after the degradation of 
the buckyball structure in a tribological loaded zone. C60 reservoirs in 
example in laser dimples may provide ongoing supply of fresh C60 
molecule cages, which can be stimulated to decor the surface again after 
the application of a certain frequency shaking.

Prime Novelty statement

The paper describes the dependence of the fullerene C60 degradation 
from the frequency of sliding. Until now, a lot of influences on C60 sta 
bility were proven, like heat, irradiation, ion bombardment, even bac 
teria influence and catalytic effects of dopants. However, the velocity of 
movement under normal load was rarely proven. A very interesting 
phenomenon was discovered: due to the lightweight structure of the 
Buckminster fullerene, a re-attraction of C60 on degenerated and 
consolidated carbon layers occurred. This observation is novel and could 
be of high importance for applications that relay on the enduring or re-
刷新ed C60 interactions like for biological and bio-oxidative effects. In
addition, the composition of gentle load tribomechanical C60 powder is compared with the C60 polymerization states of heat treated and the laser irradiated buckyball molecules.

CRediT authorship contribution statement

All authors agree to publish the work. They contributed as follow: Annor-Dereste Reisel: writing the paper; Raman spectroscopy; tribomechanical testing

Emma Freiberger: FT-IR spectroscopy

Uwe Ritter; Peter Scharf: scientific discussion and mentoring, reading the paper

Jens Moje: Providing the zirconia and the biological parameters, reading the paper

Declaration of competing interest

The authors declare that there is no conflict of interest in publication of these results.

Acknowledgement

The authors gratefully acknowledge the Federal Ministry of Education and Research, Germany for financial support of the project 13GW0401 (Acronym: Full-micro-patt). Thank is addressed to Mr. Frank Krause, KEYENCE Deutschland GmbH, Neu-Isenburg for excellent 13GW0401 (Acronym: Full-micro-patt). Thank is addressed to Mr. Frank Krause, KEYENCE Deutschland GmbH, Neu-Isenburg for excellent

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