Surface-Treated Poly(dimethylsiloxane) as a Gate Dielectric in Solution-Processed Organic Field-Effect Transistors

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Supporting Information

ABSTRACT: Poly(dimethylsiloxane) (PDMS) is a transparent and flexible elastomer which has a myriad of applications in various fields including organic electronics. The inherent hydrophobic nature and low surface energy of PDMS prevent its direct use in many applications. It is seldom utilized as a gate dielectric in solution-processed organic field effect transistors (OFETs). In this work, we demonstrate a simple method, extended ultraviolet–ozone (UVO) treatment, to modify the PDMS surface and effectively employ it in solution-processed OFETs as a gate dielectric material. The modified PDMS surface shows enhanced wettability and adherence to both polar and nonpolar liquids, which is contrary to the generally observed hydrophobic nature of UVO-treated PDMS surfaces because of the creation of polar functional groups. The morphological changes happening on the PDMS surface as a result of extended UVO treatment play a major role in making the surface suitable for all type of solvents discussed here. The contact angle measurements are used to give qualitative evidence for this observation. The modified PDMS is then used as a gate dielectric in solution-processed n- and p-channel OFETs using [6,6]-phenyl-C61-butyric acid methyl ester (PC60BM) and regioregular poly(3-hexylthiophene) (rr-P3HT) semiconductors, respectively.

1. INTRODUCTION

Poly(dimethylsiloxane) (PDMS) is a highly flexible, chemically inert, and inherently hydrophobic silicone elastomer. The high optical transparency, flexibility, and solution processability make this material attractive for many technological applications such as soft lithography, microcontact printing, microfluidics, and medical and optical devices. Because of its reversible stretchability and flexibility, PDMS is often employed in flexible electronic devices such as organic field effect transistors (OFETs), organic light emitting diodes, ac thin film electroluminescent devices, and solar cells. For the fabrication of flexible devices such as OFETs, solution-processing methods spin-coating, dip-coating, and ink-jet printing are preferred to expensive techniques such as physical vapor deposition because of ease of processibility, cost-effectiveness, and the ability to cover a large area. However, direct deposition of organic materials on PDMS by solution-processing methods is considered a challenging task because the organic semiconductors (OSCs) dissolved in nonpolar solvents show poor wettability and adherence on the PDMS surface in spite of its inherent hydrophobic nature. This has created major obstacles in making solution-processed multilayer devices on PDMS.

Surface treatments are often used to improve the wetting characteristics of polymers prior to their use in different applications. The commonly adopted techniques for PDMS surface modification are ultraviolet–ozone (UVO) treatment, oxygen plasma treatment, corona discharge, and other chemical treatments. Except for the large processing time, UVO treatment is a milder and less expensive technique compared to other surface treatment methods. It is reported that UVO treatment modifies the PDMS surface to hydrophilic with the creation of polar functional groups on its surface and hence wets the polar solvents. This does not solve the wettability and adherence issue with nonpolar solvents on the PDMS surface. In the present work, we describe a simple method called extended UVO treatment to improve the wettability and adherence of both nonpolar and polar solvents on the PDMS surface.

PDMS is commonly used as a supporting layer in flexible organic devices. Because of its good dielectric properties, PDMS is a suitable material as a gate dielectric in OFETs. In previous reports where PDMS is used as a gate dielectric, the active materials are either thermally evaporated or their single crystals are physically placed between the channels. To the best of our knowledge, PDMS is not...
used as a gate dielectric in solution-processed OFETs. Here, we employed the surface-treated PDMS as a gate dielectric in n- and p-channel OFETs by direct solution-casting of active materials, dissolved in nonpolar solvents, on PDMS. The n- and p-type semiconducting materials used in the study are [6,6]-phenyl-C61-butyric acid ester (PC_{60}BM) and regioregular poly(3-hexylthiophene) (rr-P3HT), respectively. The OFETs thus fabricated show good electrical characteristics. n- and p-channel OFETs by direct solution-casting of active materials, dissolved in nonpolar solvents, on PDMS. The n- and p-type semiconducting materials used in the study are [6,6]-phenyl-C61-butyric acid ester (PC_{60}BM) and regioregular poly(3-hexylthiophene) (rr-P3HT), respectively. The OFETs thus fabricated show good electrical characteristics.

2. RESULTS AND DISCUSSION

2.1. Effect of UVO Treatment on Wettability and Adhesion. The wetting nature of untreated PDMS to polar and nonpolar solvents is examined using contact angle (CA) measurements (Figure 1). The hydrophobicity of PDMS is evident from the large water CA (∼115°), as shown in Figure 1a. The nonpolar solvents, which are used to dissolve the semiconducting polymer/molecule used in this study, are expected to wet the PDMS surface before any surface treatment as the CAs of these solutions are small (∼20°) (Figure 1c,e). This is in accordance with the theory of wetting that a hydrophobic surface naturally gets wetted with nonpolar solvents; but we have observed that during spin-coating, the nonpolar organic solutions spilt out from the PDMS surface and failed to form a thin layer on it. This nonadhesive behavior of nonpolar solutions on the PDMS surface can be mainly due to the insufficient surface energy possessed by PDMS. Carried out UVO treatment on the PDMS surface for different exposure times and found that an extended UVO treatment for about 60 min resulted in a large reduction in the CA values (which is a measure of the surface energy) for both polar and nonpolar liquids. The water CA was reduced from 115° to 34°, and the CAs of chlorobenzene and chloroform were reduced from 20° to 3° and 7°, respectively (Figure 1d,f). The spin-coated organic solutions on the UVO-treated PDMS layer showed perfect wetting and adhesion and formed uniform thin layers (schematic representation is given in Figure 2). The high wettability of polar and nonpolar solvents on the extended UVO-treated PDMS surface point out that the PDMS surface has undergone a noticeable modification in addition to the creation of polar functionalities on its surface. Such improved wetting and adhesion can be explained based on the presence of chemical entities on the PDMS surface as well as its surface morphology.

2.2. Chemical Modification on the PDMS Surface. Attenuated total reflectance—Fourier transform infrared spectroscopy (ATR–FTIR) measurements can be used to identify different chemical functionalities present on the PDMS surface before and after UVO treatment. In Figure 3a–e, ATR–FTIR spectra of PDMS at different UVO exposure times are given. PDMS has a series of characteristic infrared bands, among these, the most intense ones were obtained for those associated with asymmetric −CH\textsubscript{3} stretching in Si−CH\textsubscript{3} (2950−2970 cm\textsuperscript{−1}); symmetric −CH\textsubscript{3} deformation in Si−CH\textsubscript{3} (1245−1270 cm\textsuperscript{−1}), stretching vibration of Si−O−Si bonds (1000−1100 cm\textsuperscript{−1}), −CH\textsubscript{3} rocking, and Si–C stretching vibrations in Si−CH\textsubscript{3} (785−815 cm\textsuperscript{−1});. These bands are common for untreated and UVO-treated PDMS. However, we observed that with increasing UVO exposure time, a broad region appeared around 3050−3700 cm\textsuperscript{−1}, as shown in Figure 3f, which corresponds to the polar functional group, hydroxyl (−OH). Also, bands corresponding to Si−O stretching vibrations in silanol (Si−OH) appeared with an increase in the UVO exposure time in the regions between 825−865 and 875−920 cm\textsuperscript{−1} (Figure S3). Simultaneously, the band corresponding to Si−C vibration was decreased (Figure S4). The reactive oxygen radicals formed during UVO exposure are responsible for the conversion of methyl (−CH\textsubscript{3}) groups to silanol (Si−OH) groups.

The increase of −OH functional
groups on the PDMS surface makes it more and more hydrophilic as the time of exposure increases.\textsuperscript{19–23}

2.3. Morphological Changes on the PDMS Surface.

The role of morphological changes in determining the wetting characteristics of PDMS was examined using scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of untreated PDMS and 60 min UVO-treated PDMS surface (Figure 4a–f). The images show that UVO treatment completely altered the surface morphology, featuring the formation of wrinkles with hills and valleys. From the AFM images, the root mean square (rms) roughness of the annealed PDMS surface was found to be \( \sim 10 \) nm. Upon extended UVO treatment, the roughness almost doubled to \( \sim 20 \) nm (roughness data are given in Table 1). The mechanism of wrinkle formation can be explained based on the high viscoelasticity of PDMS. High viscoelasticity results in mechanical stress in spin-coated PDMS thin films.\textsuperscript{10,36} Thermal curing and subsequent cooling release this stress, which results in the formation of wrinkles on the surface.\textsuperscript{10} Further, the prolonged UVO irradiation causes an increment in surface wrinkling resulting in high surface roughness.\textsuperscript{34,36} An increase in the surface roughness can also be caused by the evaporation of volatile fragments from the PDMS surface while the siloxane component is converted to silicon oxides.\textsuperscript{34,37,38}

| Table 1. Morphology Data of PDMS Films and Organic Layers Coated on Top of PDMS |
|---------------------------------|-------------------------------|-------------------------------|---------------------------|
| roughness (nm)                  | PDMS without UVO treatment   | PDMS with UVO treatment       | PDMS/P3HT                 | PDMS-PCBM                 |
| rms roughness, \( R_q \)        | 10.2                          | 20.5                          | 46.1                      | 0.396                     |
| average roughness, \( R_a \)    | 8.04                          | 16.4                          | 36.5                      | 0.31                      |

Figure 3. ATR–FTIR spectra of (a) untreated PDMS, (b) 15 min UVO exposure, (c) 30 min UVO exposure, (d) 45 min UVO exposure, (e) 60 min UVO exposure, and (f) –OH peaks at different UVO exposure time.

Figure 4. SEM and AFM images of (a,c) untreated PDMS and (b,d) UVO-treated PDMS spin-coated on a glass substrate; (e,f) show the three-dimensional view of the untreated PDMS and UVO-treated PDMS surfaces, respectively.
This is similar to the observed nanostructuring in oxygen plasma-treated PDMS.\textsuperscript{22} The reason for the high degree of wetting by nonpolar liquids on the modified PDMS surface can be attributed to the increased surface roughness.\textsuperscript{25,39} The increased surface roughness effectively increases its surface area. A low viscous liquid can easily penetrate into the deep narrow valleys, causing a reduction in the CA, and allow complete spreading,\textsuperscript{39} which then forms a thin film during spin-coating.

\subsection*{2.4. Dielectric-Semiconductor Interface Morphology.}

The dielectric–semiconductor interface of an OFET plays a crucial role in determining the channel formed between the source and drain electrodes because of the applied electric field.\textsuperscript{31,40} Any defect in the interface can cause the formation of trap states, deteriorating its operating values.\textsuperscript{31} The solvents used for dissolving the OSCs can cause swelling of the underlying dielectric, which may reduce the interface quality. The swelling ability of solvents on PDMS used in this study are in the order chloroform \textgreater cyclohexane \textgreater chlorobenzene.\textsuperscript{41} We observed that because of the moderate solubility of PDMS in chlorobenzene, the PDMS layer lying beneath the P3HT layer was negligibly affected. Though PDMS is highly soluble in chloroform,\textsuperscript{41} it did not affect the underneath layer in the device because of the high volatility of chloroform. In a bottom gate device, surface properties of the dielectric can influence the morphology and molecular organization of the OSC coated on top of it.\textsuperscript{31,42} Surface morphology of PDMS coated with the OSC solutions was evaluated using AFM and SEM images (Figure 5). The roughness data of films are given in Table 1. From the images, it is clear that the OSC layers follow the underneath wrinkled morphology of PDMS. The wrinkles are more visible in the case of the rr-P3HT layer because it is thinner than the PC\textsubscript{60}BM layer. Nevertheless, the images show that the continuity of the active layer is not lost.

\subsection*{2.5. X-ray Diffraction (XRD) Analysis.}

Besides morphology, the surface property of the gate dielectric can influence the crystallinity of the OSC layer.\textsuperscript{32} We carried out XRD analysis of the surface-treated PDMS thin film and the organic active layers coated on the modified PDMS film. The results are compared with the unmodified PDMS thin film and the untreated organic active layers spin-coated on glass substrates (Figure 6). The XRD patterns of untreated PDMS and surface-treated PDMS show similar characteristics. We observed a characteristic broad peak at a 2\(\theta\) value of 12.2\(^\circ\) in the XRD patterns of PDMS thin films before and after extended UVO treatment (Figure 6a), indicating the amorphous nature of PDMS.\textsuperscript{43} A noticeable variation in the ordering is also not observed for organic layers coated on glass and on the UVO-treated PDMS layer. The XRD pattern of rr-P3HT shows a crystalline nature with characteristic peaks around 5.6\(^\circ\) and 11.2\(^\circ\) corresponding to the crystal planes (100) and (200), respectively (Figure 6b), indicating a stacked structure.\textsuperscript{44,45} The sharp peaks at 2\(\theta\) values of 7.6\(^\circ\) and 10.7\(^\circ\) and the small distinct peaks at around 20\(^\circ\) in the XRD pattern of PC\textsubscript{60}BM indicate its crystalline nature.\textsuperscript{46} From the above observations, we conclude that the UVO-treated PDMS layer with enormous surface irregularities does not alter the basic crystallinity of the

![Figure 5](image1.png)

\textbf{Figure 5.} (a,b) SEM images, (c,d) AFM images (two-dimensional), and (e,f) AFM images (three-dimensional) of rr-P3HT and PC\textsubscript{60}BM on the UVO-treated PDMS film, respectively.

![Figure 6](image2.png)

\textbf{Figure 6.} XRD patterns of (a) PDMS before and after UVO treatment, (b) rr-P3HT thin-film on a glass substrate and rr-P3HT on the UVO-treated PDMS film, and (c) PC\textsubscript{60}BM thin-film on a glass substrate and PC\textsubscript{60}BM on the UVO-treated PDMS film.
OSCs materials coated on top of it. A broad region (from 15° to 35°) seen in all XRD data is the effect of the glass substrate on which the layers are coated. While examining the XRD patterns with and without the surface-treated PDMS layer, the peak intensity is not considered as an indication of improved crystalline nature. It is because the layered structure of PDMS can cause accumulation of OSC on the valleys and formation of a thin layer on the hills; so the intensity of peaks can vary depending on the area of focus.47

2.6. Capacitance–Voltage Measurements. The basic requirements of a gate dielectric material are its high dielectric constant ($\varepsilon_r$), high geometric capacitance ($C_i$), and the ability to produce a good quality interface with the semiconductor to ensure good field effect for proper transistor operation. With the favorable interface properties of PDMS/OSC as obtained earlier, we evaluated $\varepsilon_r$ and $C_i$ of PDMS for its application in OFETs using capacitance–voltage ($C$–$V$) measurements. The $C$–$V$ characteristics of the dielectric material evaluate the charge accumulation and discharge capabilities of the material and hence verify its capability to be used as a dielectric in transistors. We used metal–insulator–metal (MIM) (Al/PDMS/Al) and metal–insulator–semiconductor (MIS) (Al/PDMS/rr-P3HT) configurations to perform the quasi-static $C$–$V$ measurements, and the plots are shown in Figure S5. From the $C$–$V$ measurements of the MIM capacitor, the dielectric constant of the material was obtained as $\sim 2.32$ (at 1 kHz frequency), which is in agreement with the literature values ($\varepsilon_r = 2.3$–2.8 from 1 MHz to 100 Hz).26 The capacitance per unit area of the device ($C_i$) was obtained as $\sim 1.03$ nF/cm². The MIS capacitor showed typical p-type behavior with inversion–depletion and accumulation regions as the gate voltage is swept from +30 to $\sim 30$ V.

2.7. OFET Characterization. The n-channel (with PC60BM) and p-channel (with rr-P3HT) OFET devices exhibit typical current–voltage ($I$–$V$) characteristics when characterized in air and vacuum. The p-channel OFETs show saturation of drain current at low negative gate voltages but do not show a clear saturation region at high gate voltages (Figure 7a). This nature is expected because of the high level of oxygen doping in rr-P3HT, causing a significant increase in conductivity and thereby increasing the channel current. When the channel current is high enough to dominate the field effect, the channel fails to pinch-off.48,49 This effect is similar to the short-channel effect, which is a result of the thick dielectric layer compared to the channel length.50 The perfect linearity at low drain voltages indicates Ohmic contacts between the source–drain electrodes and the active material. The best value for linear mobility of p-channel OFET is found to be $6.81 \times 10^{-3}$ cm² V⁻¹ s⁻¹ and the current on/off ratio is $0.21 \times 10^3$ (at $V_{DS} = -60$ V), when the measurements are done in air. The linear mobility and current on/off ratio in vacuum are obtained as $3.38 \times 10^{-3}$ cm² V⁻¹ s⁻¹ and $0.73 \times 10^2$ (at $V_{DS} = -60$ V), respectively. The threshold voltages observed in vacuum and air are $-10$ and $10$ V, respectively. The observed change in polarity is again attributed to the increased conductivity of rr-P3HT in air because of the unintentional oxygen doping.51 The positive threshold voltage and the high off current for devices characterized in air imply that the conductivity of rr-P3HT is not negligible even in a reverse-biased condition. Oxygen doping at the exposed regions of rr-P3HT increases the conductivity of the channel, thereby increasing the off current, causing a decrease in the on/off ratio and also resulting in overestimated mobility values.51,52

The n-channel OFETs show good FET output characteristics in both air and vacuum. The $I_{DS}$–$V_{DS}$ curves are linear at low drain voltages and saturate at high drain voltages. The threshold voltage of the device is $\sim 30$ V, and the drain current is of the order of $10^{-6}$ A for a voltage range from 0 to 100 V, when characterized in vacuum. The mobility in the saturation regime is obtained as $0.81 \times 10^{-2}$ cm² V⁻¹ s⁻¹ and that in the linear regime at a low drain voltage ($V_{DS} = 8$ V) is obtained as

![Figure 7. (a) Output characteristics ($I_{DS}$–$V_{DS}$) and (b) transfer characteristics ($I_{DS}$–$V_{GS}$) of the p-channel OFET characterized in air; (c) output characteristics ($I_{DS}$–$V_{DS}$) and (d) transfer characteristics ($I_{DS}$–$V_{GS}$) of the n-channel OFET characterized in vacuum.](image-url)
6.33 × 10⁻³ cm² V⁻¹ s⁻¹ in vacuum. The current on/off ratio is of the order of 10⁴ (at V_DS = 90 V) (Figure 7cd). Unlike rr-P3HT, the PC₆₀BM semiconductor material degrades in an ambient atmosphere, and the OFET device performance is affected. The output characteristics of the p- and n-channel OFETs in vacuum and air, respectively, are shown in Figure S6. The characteristic values of both n- and p-channel OFETs are listed in Table S1 of the Supporting Information. The transfer characteristics of both OFET devices show a small hysteresis as shown in Figure S7. In OFETs, the hysteresis can occur because of several reasons, such as charge-carrier trapping close to the channel, presence of mobile ions in the dielectric, or slow polarization of the dielectric.53 As discussed earlier, the increased roughness of the PDMS layer leads to the creation of wrinkles in the channel region, which may act as charge-carrier traps.31 We obtained hysteresis-free characteristics with slow sweeping rates (Figure S7). This observation suggests the presence of trapped majority or minority charges in the channel near the semiconductor/dielectric interface. Even though the roughness in the dielectric is detrimental to the dielectric/semiconductor interface quality, the transistor performance is not affected by this factor. The mobility values obtained from the OFET devices are comparable to the reported values for rr-P3HT and PC₆₀BM semiconductors. The reasonable device performance, even with the wrinkled morphology of the PDMS dielectric, can be attributed to the presence of a strong localized electric field at the valleys of the wrinkles.54

3. CONCLUSIONS

In summary, we modified the surface of PDMS by using extended UVO treatment and enabled the adhesion of both polar and nonpolar solvents on its surface. The presence of hydroxyl groups and the wrinkled morphology together contributed to the increase in its surface energy and thereby improved the wetting and adhesion. The modified PDMS was then utilized as a gate dielectric in solution-processed active layer-based OFETs. The n- and p-channel OFETs using solution-processed OSCs, PC₆₀BM and rr-P3HT, showed characteristics typical for the corresponding OFETs. The present study demonstrates the potential of PDMS as a gate dielectric in solution-processed FETs and suggests its applicability in solution-processed multilayer flexible devices.

4. EXPERIMENTAL METHODS

4.1. Materials. PDMS (Sylgard 184) along with the curing agent were purchased from Dow Corning. The semiconductors, rr-P3HT and PC₆₀BM, were procured from American Dye Source Inc.

4.2. PDMS Surface Modification and Surface Property studies. PDMS, mixed with the curing agent in a 10:1 ratio and diluted in cyclohexane (PDMS/cyclohexane = 1:2), was spin-coated onto cleaned glass substrates at a speed of 6000 rpm. The thickness of the layer was found to be ~2 μm (measured using an Alpha-Step D-600 Stylus Profiler, KLA-Tencor). After thermal annealing for 30 min at 150 °C, the layers were treated with a UVO cleaner (UVOCS, USA) for different time durations. A low-pressure quartz-mercury vapor lamp of output power 9 mW/cm², which generates UV emissions in the 254 and 185 nm range, was used as the UV source. CA measurements (CA Meter, Holmarc) were done with water and organic solutions of rr-P3HT and PC₆₀BM by dissolving them in chlorobenzene and chloroform solvents, respectively. The method used to qualitatively find the wetting nature and surface energy from CA measurements is given in the Supporting Information (Figure S1). The FTIR–ATR spectra of untreated PDMS and UVO-treated PDMS at different exposure times were measured using a Bruker Alpha-E FTIR spectrometer equipped with a ZnSe crystal. The surface morphologies of untreated PDMS (only annealed at 150 °C), UVO-treated PDMS, and OSC coated on PDMS were investigated using AFM (Bruker multimode 8 AFM) and SEM (Nova NanoSEM 450 FEI) techniques. The effect of UVO treatment on the PDMS surface and thereby on the ordering of the OSC layer spin-coated on PDMS were investigated using XRD (Empyrean, PANalytical XRD instrument with Cu Kα radiation) measurements.

4.3. Dielectric Property Studies. The capacitance–voltage (C–V) measurements of the PDMS dielectric were carried out in its MIM (Al/PDMS/Al) and MIS (Al/PDMS-P3HT) configurations at 1 kHz. The measurements were done using a Keithley SCS 4200 semiconductor parameter analyzer.

4.4. Fabrication and Characterization of OFETs. OFET devices were fabricated in the bottom gate-top contact configuration (Figure S2) on cleaned glass substrates with rr-P3HT and PC₆₀BM as active layers and extended UVO-treated PDMS as the gate dielectric. Thermally evaporated aluminum of thickness ~80 nm served as the gate electrode (monitored using INFICON quartz thickness monitor). The PDMS film spin-coated on the Al gate electrode was then cured at 150 °C for 30 min and UVO-treated for about 60 min before semiconductor coating. The optimized values of concentration, spin speed, and annealing temperatures were used for active layer coating. The OSCs, rr-P3HT, and PC₆₀BM were spin-coated on PDMS from a solution of 10 mg/mL in chlorobenzene and 20 mg/mL in chloroform, respectively, at a spin speed of ~800 rpm. The rr-P3HT layer was annealed at 110 °C for 30 min, and PC₆₀BM was annealed at 60 °C for 10 min. The thicknesses of rr-P3HT and PC₆₀BM were 60 and 250 nm, respectively. Gold source–drain electrodes were evaporated onto the OSC layers leaving a channel length (L) of 50 μm between the source and drain electrodes, keeping the channel width (W) at 2 mm.

The OFET devices were fabricated in a nitrogen atmosphere. The characterization was done in air as well as in vacuum conditions using a Keithley SCS 4200 semiconductor parameter analyzer. We calculated the field-effect mobilities (μₘₐₓ and μₘₜₜ) of OFETs in the linear and saturation regimes of operation using following eqs 1 and 2, respectively:

Current in the linear regime

\[ I_{DL} = \frac{W}{L} \mu_{lin} C_i (V_{GS} - V_{TH}) V_{DS} \]  

(1)

Current in the saturation regime

\[ I_{DL} = \frac{W}{2L} \mu_{sat} C_i (V_{GS} - V_{TH})^2 \]  

(2)

where W (2 mm) and L (50 μm) are the transistor channel width and length, respectively, \( V_{TH} \) is the threshold voltage, and \( C_i \) is the capacitance per unit area of the PDMS gate dielectric.
Description of the CA measurement, schematic of the contact angle of a liquid on a solid surface showing good wettability and low wettability, schematic of the transistor in the bottom gate-top contact configuration and the chemical structures of the dielectric and semiconductor materials used, ATR–FTIR spectra of PDMS, C–V characteristics of PDMS in the MIM and MIS configurations, output and transfer characteristics of p- and n-channel OFETs, and summary of the electrical performances of the OFETs at different operating conditions (PDF)

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