Supporting Information

Introducing Optical Nonlinearity in PDMS using Organic Solvent Swelling

Sudhakara Reddy Bongu[1,2], Maximilian Buchmüller[1,2], Daniel Neumaier[2]*, Patrick Görrn[1,2]*

[1]Chair of Large Area Optoelectronics, University of Wuppertal, Rainer-Gruenter-Str. 21, 42119 Wuppertal, Germany.

[2]Wuppertal Center for Smart Materials and Systems, University of Wuppertal, Rainer-Gruenter-Str. 21, 42119 Wuppertal, Germany.

E-mail: goerrn@uni-wuppertal.de

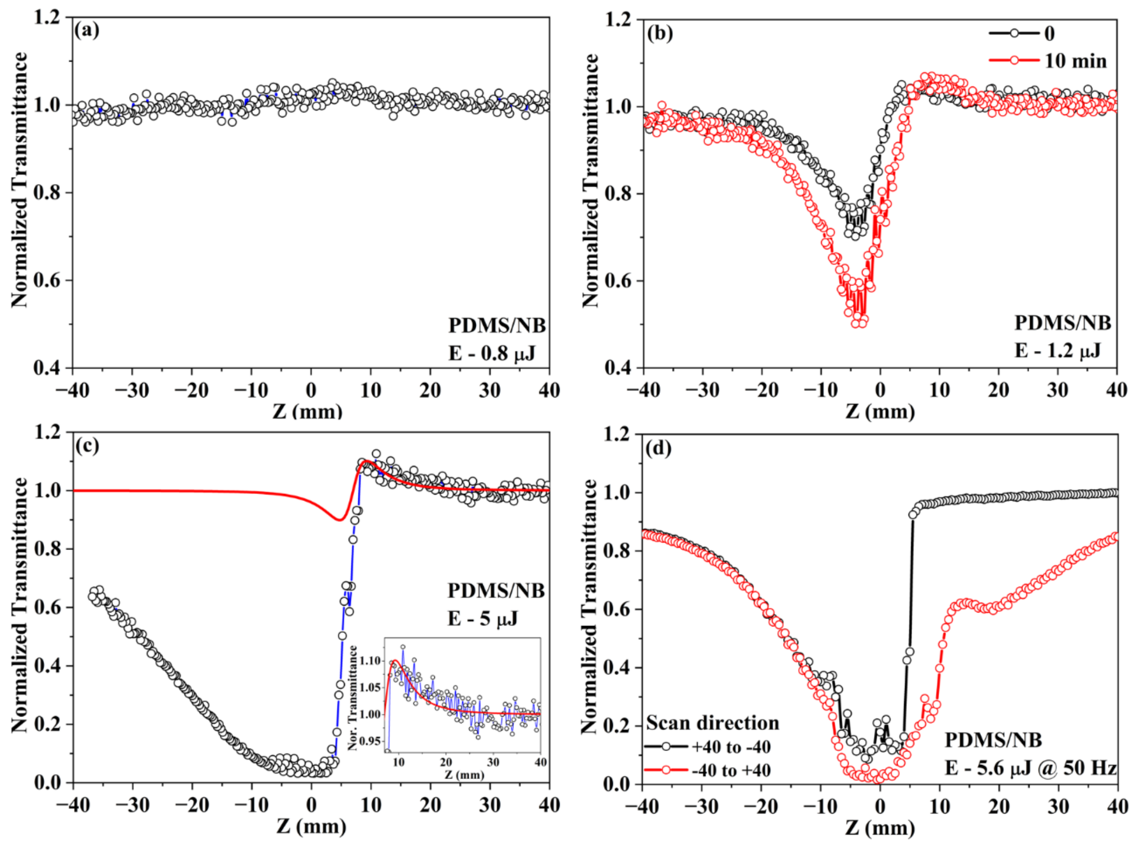

Figure S1: Closed aperture Z-scan profiles of PDMS/NB under various experimental conditions. (A)-(C): CA Z-scan profiles of PDMS/NB at 10 Hz repetition rate and a pulse energy of 0.8 µJ (A), 1.2 µJ (B), and 5 µJ (C); (D): Closed aperture Z-scan profiles of PDMS/NB at a repetition rate of 50 Hz and a pulse energy of 5.6 µJ.

At low pulse energies, as illustrated in Figure S1a, the PDMS/NB composite material shows linear behaviour. At higher pulse energies, e.g. shown in Figure S1b for 1.2 µJ pulse energy, the samples exhibit nonlinearity, but the profiles show artefacts close to the focus (Z = 0 mm). While in all measurements shown in the manuscript, the scan profiles are independent from the scan direction, this is not the case for the following measurements. The scan shown in S1b starts at +40 mm and ends at -40 mm. During the scan, the signal first increases at a position around 10 mm, which can be attributed to the Kerr effect, see red fit curve in Figure S1c. However, when further moving the sample towards the focus, the signal suddenly drops due to strong beam distortions caused by thermal effects. Therefore, a proper fit for determining the nonlinear optical material parameters is not possible. If we repeat the scan at the same sample position (red curve in Figure S1b), the drop of the signal becomes even stronger, which hints to an accumulating effect of material degradation.

If we further increase the pulse energy (S1c) and the repetition rate (Figure S1d), the artefacts become even more pronounced and it becomes clear that a permanent photo-induced degradation of the material takes place during the measurement.

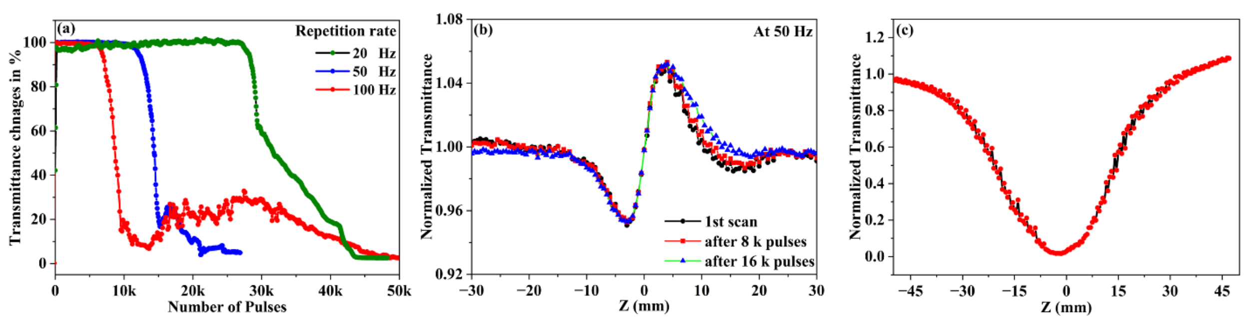

Figure S2: Long-time stability investigations. a) transmittance of PDMS/TL under intense laser illumination; b) comparative z-scan profiles after different illumination durations at a repetition rate of 50 Hz ; c) z-scan profile after the laser-induced damage threshold has been reached.

To investigate the long-term stability of the samples, we have performed additional experiments to assess potential material alterations caused by exposure to intense laser light. As an example, we have chosen PDMS/TL, because of its promising nonlinear optical properties, as described in the manuscript. A z-scan measurement was initially performed on a freshly fabricated sample. Subsequently, the sample was positioned at the focal point (Z_0) with maximum intensity, while monitoring transmittance. Over the course of up to 27,000 pulses the transmittance remained constant. However, a subsequent decline in transmittance was observed, indicating a laser-induced damage effect (see Figure S2a). Remarkably, the onset of this decline depends on the laser's repetition rate, suggesting an accumulating effect that intensifies with the heat introduced to the sample.

To further investigate the destruction mechanism, additional z-scan measurements were conducted. When the intense laser illumination was switched off before any transmittance change, the z-scan result was the same compared to the results obtained immediately after fabrication (see Figure S2b). Interestingly, when high-intensity illumination was switched off before laser-induced damage, a brief cool-down period of only a few minutes was sufficient for the material to return to its post-fabrication behavior. We have repeated this procedure multiple times without observing any change in this behavior. This implies that, as long as the sample remains below a critical heat threshold, the material shows stability on a much longer time-scale. Conversely, if a z-scan measurement was performed after transmittance alteration, the result exhibited significant changes (Figure S2c).

Notably, the observation that pure PDMS exhibits a lower damage threshold than the composite suggests the influence of additional parameters on the laser-induced damage behavior, such as the contact of the material with atmosphere. Thus, the damage mechanism appears to be a complex interplay of individual parameters (laser illumination, temperature, exposure to atmosphere) rather than a simple superposition. Investigations on such dependencies will be subject of future work.