Supporting Information

Observing Phthalate Leaching from Plasticized Polymer Films at the Molecular Level

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SFG and FTIR Experimental Details

The sum frequency generation (SFG) vibrational spectrometry set up used in this study (EKSPLA) has been reported in detail previously. The output of the Nd:YAG laser is a 1064 nm near-IR beam (20Hz, 20 ps). The visible input 532 nm beam is generated by frequency-doubling a part of this 1064 nm IR beam. The mid-IR input beam is generated from a nonlinear optical box and can be tuned from 1000 cm\(^{-1}\) to 4300 cm\(^{-1}\). For all the SFG experiments performed here, the incident angles of the visible and the IR input beams were 60° and 55° with respect to the surface normal, respectively. The diameters of the two input beams at the surface were ~500 µm. The SFG spectra were collected in the ssp (s-polarized output, s-polarized visible input, and p-polarized IR input) polarization combination. Both silica and CaF\(_2\) windows were used as substrates for sample deposition. The results obtained from the samples on silica and CaF\(_2\) windows were similar, therefore only SFG results obtained from samples on CaF\(_2\) windows are shown in this paper.

A Nicolet Magna 550 FTIR spectrometer was used to take FTIR spectra. Each spectrum displayed in this paper was collected with a resolution of 4 cm\(^{-1}\), 128 scans, and in the wavenumber range from 900 to 3200 cm\(^{-1}\). The CaF\(_2\) windows were used as sample substrates. The FTIR sample chamber was purged with nitrogen gas during and before measurements. A blank spectrum of CaF\(_2\) was obtained as background before each measurement to compensate for possible humidity changes and carbon dioxide variation in the chamber.

**Discussion on Evaporation of DEP**

We suggest that the fast volatilization of DEP molecules under vacuum can be attributed to the low boiling point (BP) of DEP molecules under low pressure during the pumping process. The
BP of DEP is 295 °C under 1 atm, but Buckingham et al. reported that the BP of DEP decreases to 430 K (157 °C) at 0.013 bar.[3] During our plasma treatment, the pressure in the sample chamber is only 200 milli-torr (~10⁻⁴ bar). Therefore the DEP BP should be much lower than 430 K. In this case DEP may easily migrate to the surface and volatilize during plasma treatment. Thus the pumping process itself likely induces DEP leaching. On the other hand, DEP is more hydrophilic than DBP since it contains shorter carbon chains, so the interaction between DEP and PVC would be weaker than that between DBP and hydrophobic PVC. From this point of view, DEP should leach out more easily from PVC than DBP.

Figure S1. FTIR spectra of pure DEP film before and after vacuum pumping, indicating that almost no DEP molecules remain on the substrate surface after pumping. These results illustrate that vacuum-involved techniques such as plasma treatment are not suitable for preventing DEP leaching from plastics.

Additional Spectra from the PVC/DBP Samples
Figure S2. FTIR spectra of PVC/DBP samples without (a) and with (b) plasma treatment after annealing at 70 °C overnight.

The FTIR spectra of PVC/DBP samples without plasma treatment after heating at 70 °C overnight only differ in intensity, all containing spectral features similar to pure PVC spectra (Figure S2a). This is very different from the spectra collected from the samples treated with oxygen plasma for 10 s (Figure S2b). In Figure S2b, although the FTIR spectral features of PVC/DBP samples with lower bulk DBP concentrations are also very similar to those of the pure PVC spectra, as the bulk concentration of DBP increases to 70 wt%, the collected FTIR spectra contain phthalate signatures (2963 cm\(^{-1}\) and 1280 cm\(^{-1}\) peaks). These results indicate that a short-time oxygen plasma treatment cannot completely prevent DBP leaching from the PVC/DBP matrix to the surrounding environment.
Figure S3. ATR-FTIR spectrum detected from a ZnSe crystal with deposited DBP molecules. The molecules deposited on ZnSe from the air after migrating from a 70 wt% DBP sample heated at 70 °C overnight.

Figure S4. FTIR spectra of PVC/DBP samples without (a) and with (b) plasma treatment after annealing at 30 °C overnight.
Figure S4 demonstrates that the FTIR spectra of DBP/PVC samples after annealing at 30 °C for 14 hours with and without plasma treatment are similar. In this case, FTIR is not sensitive enough to detect the DBP leaching.

Figure S5. FTIR spectra collected from un-treated and plasma-treated PVC/DBP samples with 0 wt% DBP, i.e. PVC (a), 5 wt% DBP (b), 15 wt% DBP (c), 30 wt% DBP (d), 70 wt% DBP (e), and 100 wt% DBP (f) before and after annealing at 30 °C for 2 hours.
Figure S6. SFG spectra of the sample A’s after annealing at 30 °C for 2 hours without (a) and with plasma treatment for a short time.
Figure S7. SFG spectra of sample B’s after annealing 5 wt% DBP (a), 15 wt% DBP (b), 30 wt% DBP (c) and 70 wt% DBP (d) samples at 30 °C for 2 hours.
Figure S8. FTIR spectra collected from PVC/DBP samples with and without plasma treatment for 0 wt% DBP, i.e. PVC (a), 5 wt% DBP (b), 15 wt% DBP (c), 30 wt% DBP (d), 70 wt% DBP (e), and 100 wt% DBP (f) before and after annealing at 70°C for 2 hours.
Figure S9. SFG spectra of the samples A’s after annealing at 70 °C for 2 hours: (a) without plasma treatment; (b) with plasma treatment for a short time.

Figure S10. SFG spectra of the sample B’s after heating at 70 °C for 2 hours: 5 wt% DBP (a), 15 wt% DBP (b), 30 wt% DBP (c) and 70 wt% DBP (d) samples for 2 hours.
References:

