SUPPORTING INFORMATION

Polymer Encapsulation of an Amorphous Pharmaceutical by initiated Chemical Vapor Deposition for Enhanced Stability

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iCVD setup

Polymerization by initiated chemical vapor deposition (iCVD) is performed in custom-made vacuum reactor. The cylindrical chamber (height 5.5 cm, diameter 36 cm) is pumped by a Duo 5M rotary vane pump (Pfeiffer Vacuum, Germany) and the process pressure is regulated by a throttle valve (MKS Instruments, USA). A removable quartz glass lid allows for *in situ* thickness control via laser interferometry (He-Ne laser with $\lambda = 633$ nm, Thorlabs, USA). The chamber houses a resistively heated filament array of 12 parallel nickel-chromium wires (Goodfellow, UK), which are mounted 2.5 cm above the reactor floor. The substrate temperature is regulated by an Accel 500 LC heater/chiller (Thermo Fisher Scientific, USA) to ± 2°C, as monitored by type K thermocouples (Omega Engineering, USA). The monomers are stored in glass jars at constant temperatures (PFDA and EGDMA at 80 °C, HEMA at 75 °C and MAA at 70 °C) and can be flown into the reactor through a heated mixing line (held at 90 °C). Both initiator and nitrogen enter separately the chamber at ambient temperature. The individual flow rates were manually set by needle valves (Swagelok, USA) or mass flow controllers (MKS Instruments, USA). The individual process parameters used in this work are stated in Table S1.

Table S1. Deposition parameters for the individual polymer coatings. The flow rates of the monomers (F_{mono}), crosslinker (F_{EGDMA}), the initiator (F_{TBPO}) and nitrogen (F_{N2}) are summarized together with the filament ($T_{filament}$) and substrate ($T_{substrate}$) temperatures. During deposition, the pressure (p) was constant.

	F_{mono} [sccm]	F_{EGDMA} [sccm]	F_{TBPO} [sccm]	F_{N2} [sccm]	$T_{filament}$ [°C]	$T_{substrate}$ [°C]	p [mTorr]
p-HEMA	0.75 ± 0.05	0.03 ± 0.05	0.80 ± 0.05	3.0 ± 0.1	310 ± 10	30 ± 2	350 ± 10
p-MAA	0.80 ± 0.05	0.03 ± 0.01	0.80 ± 0.05	3.0 ± 0.1	240 ± 10	25 ± 2	500 ± 10
p-PFDA	0.15 ± 0.03	-	0.60 ± 0.05	6.0 ± 0.1	240 ± 10	30 ± 2	800 ± 10

Clotrimazole double peak

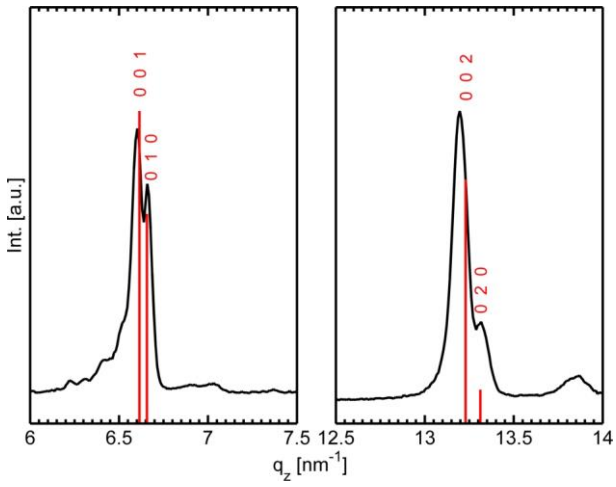

Figure S1. Image section of the X-ray diffraction pattern of clotrimazole, encapsulated by p-HEMA, after 24 hour storage at 70 °C. The red bars indicate the positions and the intensities of the 001, 010 and higher order reflections of an ideal clotrimazole powder.

Crystalline clotrimazole layers

For the identification of the wrinkling effect, a crystalline sample of clotrimazole was prepared. On this crystalline sample, a 200 nm p-HEMA layer was deposited (Figure S2, left) which results in a surface structure that is dominated by the underlying clotrimazole crystals. On heating to 160°C, slightly above the melting temperature of clotrimazole (T_m = 150°C), all crystals disappeared but the formation of wrinkles is clearly visible (Fig. S2, middle). After storing this sample at 70°C for 48h, crystallization is again observed, but different to the initial film, surface wrinkling prevails.

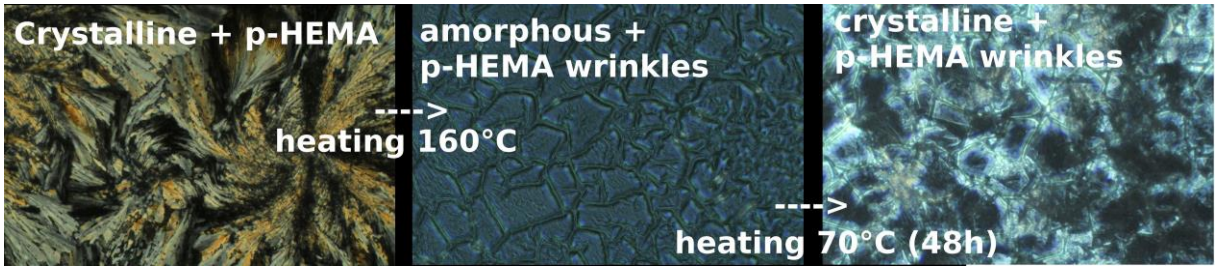

Figure S2. Crystalline clotrimazole coated with a p-HEMA layer (left), the same sample heated above 160°C and rapidly cooled to room temperature (middle) and the sample stored at 70°C for another 48h.