Low-Distortion, High-Strength Bonding of Thermoplastic Microfluidic Devices Employing Case-II Diffusion-Mediated Permeant Activation

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Results and Discussion Supplementary Information

Case-II permeation in Zeonor™ 1060R

We have demonstrated the existence of case-II mediated permeation in Zeonor™ by two independent methods. The first is adapted directly from pioneering studies of case-II diffusion in PMMA.[1] The technique employs an iodine stain to enhance visualization of the case-II swelling front in bulk Zeonor™ sheets and allows determination of the bulk case-II front velocity. The second method uses a QCM approach to confirm the linear permeant mass uptake with time characteristic of case-II diffusion. QCM experiments are also used to measure thin-film case-II front velocities and equilibrium permeant uptakes for a series of permeant mixtures.

Fig. 1 illustrates typical characteristics of case-II permeation. Zeonor™ sheets were immersed in an 80:20 wt% mixture of ethanol:decalin containing 0.5 wt% iodine for selected time intervals, then rinsed, dried, and prepared for examination. When viewed in cross-section (Fig 1a-d), a sharply-defined front is observed to migrate into the sheets. Front migration is linear with time for depths up to 75 μm; slowing sets in at greater depths (Fig 1e). Slowing of the case-II front velocity (ν_o) is observed in many systems and is associated with diffusional lag of higher molecular weight permeants in the swollen outer portions of the sheet.[3] Front slowing has been incorporated in recent theoretical treatments.[4] A positive non-zero intercept is observed in Fig. 1e, suggesting that consistent slight smearing or thermal distortion of the permeated layer occurs during sample preparation. A least-squares fit yields a bulk v_o of 0.12 μm/min. This is somewhat slower than the rate measured in a thin film by QCM. The measured bulk v_o may slightly overestimate the true bulk v_o due to residual swelling distortions in the stained regions. However, the long sample preparation time and sample heating during epoxy cure make it unlikely that residual trapped permeant contributes significantly to any swelling distortion.

QCM methods have been used widely to characterize interactions of glassy polymers with liquids.[5] The well- known Sauerbrey relationship[2,6] (1) is useful for relating quartz resonant frequency shifts (Δf) to changes in polymer film mass (Δm). In practice, crystal-dependent constants f_o (the resonant frequency of the unloaded crystal), μ_q, and ρ_q (the shear modulus and density of quartz, respectively), can be replaced by an integral sensitivity constant C_f. The quantity C_fA (where A is the piezoelectrically active area) may be determined experimentally for a given crystal geometry and film composition. QCM analysis is further simplified in this case by

$$\Delta f = (-2f_o^2/A(\mu_q\rho_q)^{1/2})\Delta m = -C_fA\Delta m \qquad (1)$$

$$|\Delta f_{p,\,tot}/\Delta f_{d,\,tot}| = |\Delta m_{p,tot}/\Delta m_{d,\,tot}| = m_p/m_o \qquad (2)$$

comparing $\Delta f_{p,\,tot}$ observed at full permeation of one Zeonor™ film in a swelling medium with $\Delta f_{d,\,tot}$ associated with full dissolution of an identical film in a solvent. So long as thicknesses are carefully controlled, the ratio of frequency shifts directly yields the equilibrium mass uptake

m_p/m_o (where m_p is the mass of permeant and m_o is the initial mass of polymer) of the swollen film (2). Front velocities v_o are determined from the time required for full swelling of a film of known thickness, using the linear mass uptake regime to correct for initial inhibition and to extrapolate the endpoint time, if necessary.

Representative QCM measurements of Zeonor™ swelling and dissolution are shown in Fig 1f. On immersion in 80:20 wt% ethanol:decalin, a linear decrease in resonant frequency ($-\Delta f > 0$) is observed as the case-II front moves through the film. As the front reaches the quartz surface, the resonant frequency becomes constant, indicating the presence of an equilibrated stable swollen film. Continued monitoring of the crystal showed that the film is stable for at least several hours following complete swelling. On immersion in cineole, a solvent for Zeonor™, a linear increase in resonant frequency ($-\Delta f < 0$) is observed as the film dissolves. On full dissolution, the resonant frequency again stabilizes. We do not know of any specific reason why the time to complete swelling in ethanol:decalin and the time to complete dissolution in cineole are approximately the same.

Table 1 summarizes case-II permeant characteristics measured by QCM for several decalin mixtures, including solution and vapour-phase permeation. Front velocity v_o is highly sensitive to composition. At 20 °C, v_o of an 80:20 wt% ethanol:decalin mixture is convenient for implementing a bonding process: approximately 1 μm of Zeonor™ is permeated per 7 min. of immersion time.

Equilibrium permeant uptake increases with increased decalin concentration. As discussed below, the equilibrium uptake does not reflect the composition of the activated layer during bonding. For all mixtures of decalin and ethanol presented here, linear mass increase is followed by a sharp transition to a plateau as illustrated in Fig. 1f. A minor induction period is observed prior to swelling for the 85:15 mixture. Measurements are reproducible to ± 2.5% for both front velocity and equilibrium uptake determinations of the solution-based experiments.

For an 80:20 wt% ethanol:decalin mixture, v_o as determined by QCM for a thin film is approximately 50% faster than v_o observed in bulk measurements. The difference is likely to arise from the dissimilar thermal histories of the Zeonor™ samples or from geometric effects that produce similar retardation of bulk case-II rates relative to thin-film case-II rates for PMMA.[7] For generating controlled bonding layers with thicknesses on the order of 1-2 μm, the difference between the measured rates is of little consequence.

None of the experiments reported here directly address the composition of the permeant within the swollen Zeonor™ film. Decalin is a good solvent for Zeonor™, while ethanol is a non-solvent. Preferential absorption of decalin into the swollen layer appears likely, but instances of case-II diffusion in other polymers in the presence of solvent/nonsolvent mixtures tend to be complex.[8] This issue requires further study to resolve.

While a series of Fickian and anomalous diffusion cases have recently been documented in the COC Topas™ 6013,[9] the examples presented here represent, to the best of our knowledge, the first documentation of case-II diffusion in a COC. Given the glassy nature of Zeonor™, observation of case-II behavior should not be surprising. In comparison, more conventional polyolefins are semicrystalline and generally display Fickian diffusivity.[10]

References

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Table 1 Case-II Uptake of Decalin Mixtures in Zeonor™ 1060R thin films at 20 ^{o}C measured by QCM except as noted.

Composition	Front Velocity v_o (μm/min)	Equilibrium Uptake (g permeant/g polymer)
85:15 Ethanol:decalin	0.005	0.28
80:20 Ethanol:decalin	0.18	0.43
80:20 Ethanol:decalin[a]	0.12	*not determined*
75:25 Ethanol:decalin	0.81	0.63
Decalin vapor[b]	0.085[b]	0.6[b]

[a] Bulk measurement in 1.6 mm thick Zeonor™ 1060R: see Fig. 1. Unlike the QCM thin film measurements, bulk sample measurements were not carried out to complete uptake and thus an equilibrium uptake was not calculated.

[b] Vapour uptake is anomalous but approximates case-II behaviour; values are estimates of the case-II component of permeation: see Fig. 2, main article.

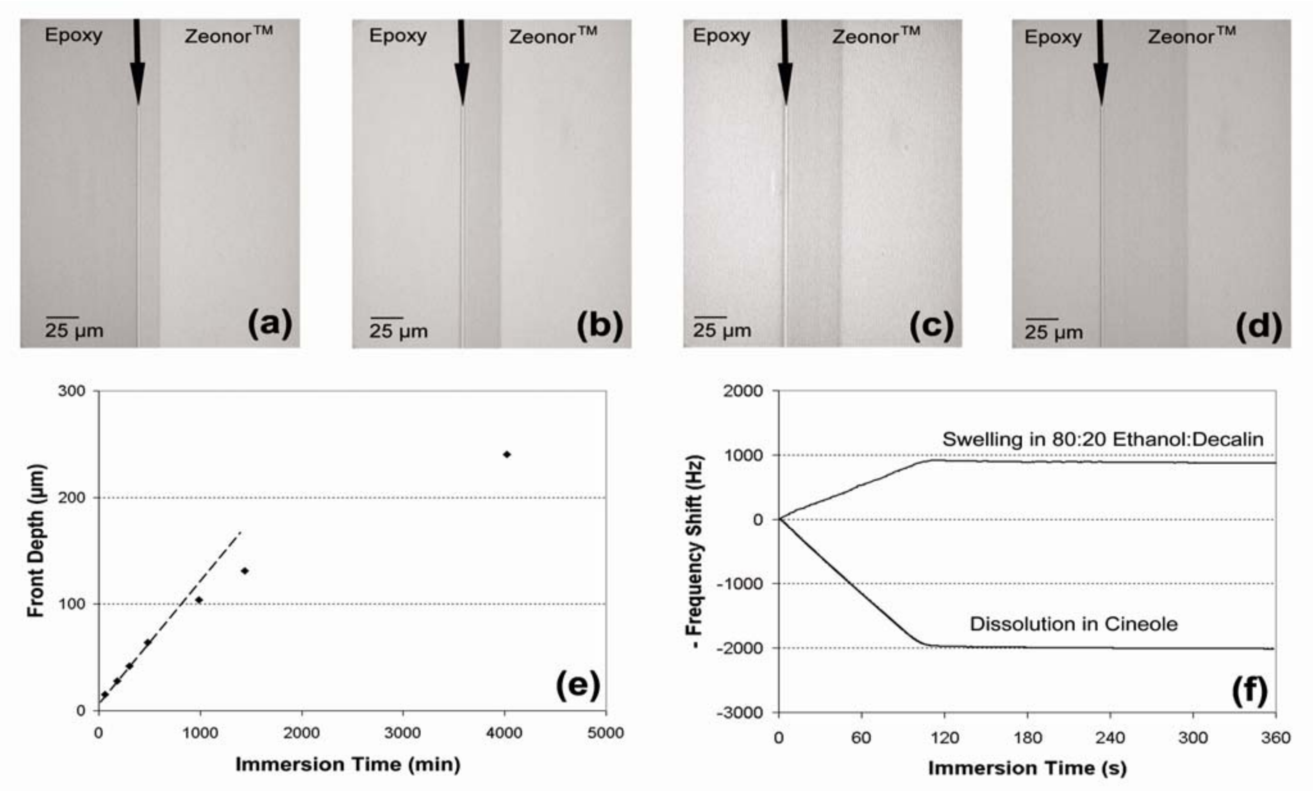

Figure 1: Case II permeation of an 80:20 wt% ethanol:decalin mixture into Zeonor™ at 20 ºC. Optical micrographs (a)-(d) show propagation of the case II front into bulk Zeonor™ at t = 60, 180, 300, and 480 minutes, respectively, as visualized by iodine-enhanced staining. Arrows indicate epoxy-Zeonor™ interfaces. Permeation is from left to right starting at the arrows. (e) Plot of front depth vs. immersion time for bulk Zeonor™. Front propagation is linear with time to a depth of approximately 75 µm; slowing sets in at greater permeation depths. (f) Plot of QCM frequency shift measurements of swelling response in 325 nm thick Zeonor™ films to immersion in 80:20 wt% ethanol:decalin (top trace) and dissolution in cineole (bottom trace).