Supplementary Information (SI) for Soft Matter.

SUPPLEMENTARY MATERIAL

Bubble growth in a confined heated polymer: the example of safety glass

THE ROYAL SOCIETY OF CHEMISTRY: SOFT MATTER

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Rheology of PVB polymers

We surveyed the rheological behavior of RB41, QS41, and DG41 in the frequency space using oscillatory shear rheometry (ω=0.1-10 rad/s), under small deformation (ϒ=0.01%), and between 20-140°C. From the time-temperature master curves, we derived two characteristic times t_e, t_d. The former denotes the Rouse relaxation, and thus, the transition from the glassy to the rubbery state. The latter is the characteristic time of reptation of the polymer chains and signals accordingly the rubbery-to-viscous transition. These times scale with temperature and are thus used to create a time-temperature diagram for the polymers under small strain (Figure S1A-C). See Arauz-Moreno, Piroird, & Lorenceau (2022) for information on the experimental protocol, sample preparation, and relevant equations used to create the diagrams.

Concerning the Rouse transition, for QS41 (tri-layer) we found two relaxation times (25°C) $t_{e,A} \approx 19.3\ s$ and $t_{e,B} \approx 0.12\ s$, which signal that two layers are identical in relaxation, while the third one is not. The longest Rouse time in this case was fairly identical to the one for RB41 ($t_e \approx 20\ s$) which suggests that the layers in question may be of identical composition. The Rouse time for DG41 was in the order of $\approx 3.45 \times 10^5\ s$, which reflects the reduced amount of plasticizer in this blend, and hence, its stiffer nature. In terms of the reptation times, the blends exhibited widely different values of $t_d = 10^{12} s$ (DG41), $10^9 s$ (RB41), and $10^8 s$ (QS41).

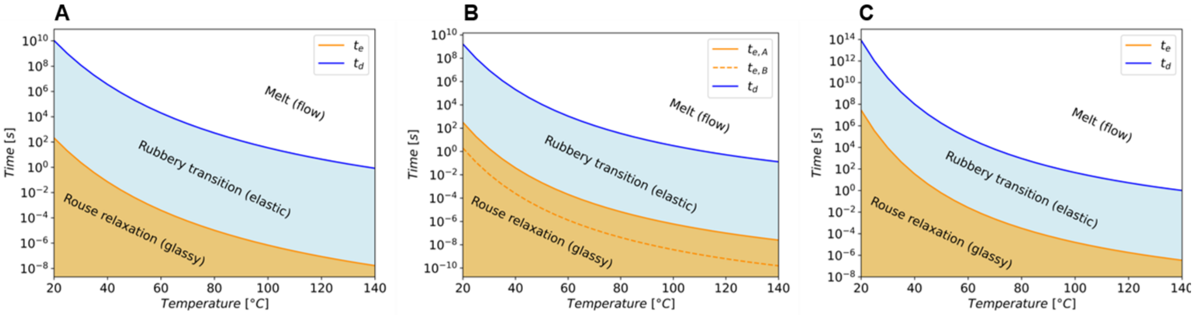


Figure S1: Time-temperature state diagram for PVB polymers. ***A*** *RB41,* ***B*** *QS41,* ***C*** *DG41. The transition is delineated by t_e and t_d, the Rouse and reptation time of the polymer chains respectively.*

The generalized time-temperature Maxwel model for RB41 (and RB11 for they have the same chemistry), includes 10 spring elements, with an equal number of relaxation times (see eq. 21 in the main paper). Table S1 presents the constants while Figure S2 provides a comparison between the Maxwell model and the associated data whence it was originally derived in Arauz-Moreno, Piroird, & Lorenceau (2021). As seen from the latter figure, the model is strictly valid for elasticities between $\sim 5 \times 10^6 < G(t) < \sim 10^1$ Pa, which is sufficient to describe the bake test, both in terms of timescale and temperature.

Table S1: Maxwell model constants at T^*=25°C

G_i[Pa]	λ_i[s]	G_i[Pa]	λ_i[s]
3.40E+06	3.34E−01	8.42E+04	1.52E+08
8.09E+05	6.56E+00	3.65E+04	1.23E+09
1.92E+05	4.59E+02	1.14E+04	8.90E+09
1.13E+05	2.56E+05	2.38E+03	6.69E+10
1.08E+05	1.02E+07	4.23E+02	4.84E+11

C_1=15.32, C_2=79.05°.

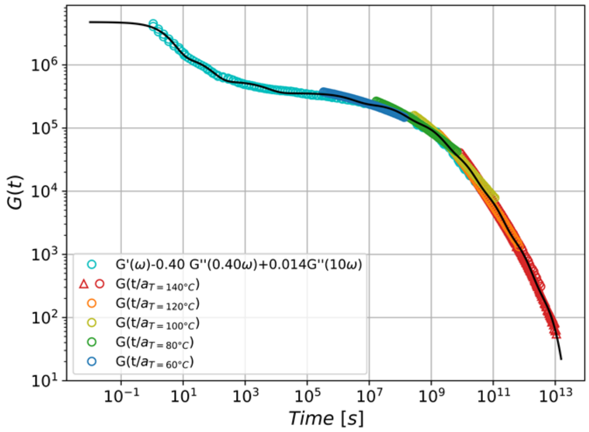


Figure S2: — Maxwell model versus experimental PVB relaxation data in the time domain from shear rheometry at 20°C. ○ Relaxation data obtained by interconverting the storage and loss moduli in the frequency space (ϒ=0.01%, ω=0.1-10 rad/s, T=20-140°C), ○Δ○○○○ Relaxation data measured directly in the time domain at 140, 120, 100, 80, 60°C. The curves were shifted via a shift factor a_T in accordance with the principle of time-temperature superposition to generate the master curve of the relaxation (fig. 4B in the main text). See Arauz-Moreno, Piroird, & Lorenceau (2021) for full details on the model and associated experimental data.

Water content post lamination

The amount of water dissolved in the PVB bulk can be measured along the lamination process via near infrared (NIR) spectroscopy. It simply suffices to take a reference spectrum of glass without PVB (preferably of equivalent thickness as the sample to be measured), and then scan either a pre-press or a finished sample of laminated safety glass. The qualitative amount of water is $r_{abs} = p_{h2O}/p_{PVB}$, where p is the transmission peak for water (1873-1925 nm) and PVB (1609-1710 nm) respectively (figure S3A). See Arauz-Moreno, Piroird, & Lorenceau (2023) for further details.

As shown in figure S3B, post autoclaving, the amount of water from the pre-press to the finished sample is roughly the same, except around the edges. In this respect, water is lost because of mass diffusion. The affected length is only a couple of millimeters, however.

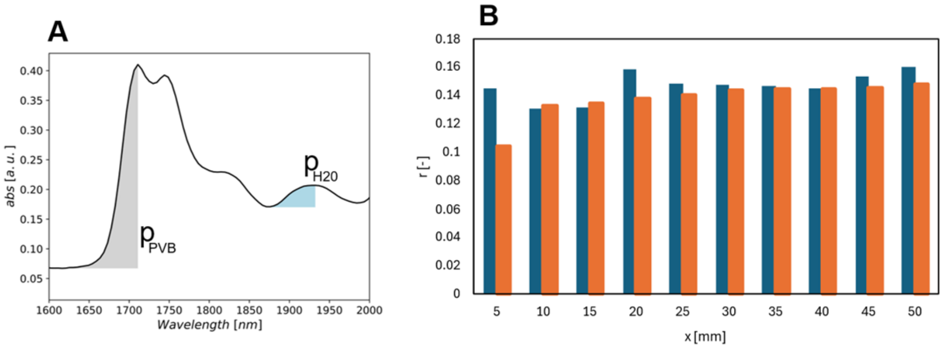


*Figure S3: **A** Typical NIR spectrum in a glass sample with PVB. **B** NIR spectra of a sample, before (blue bars) and after autoclaving (orange bars). x=0 is the edge of the glass sample. Water is lost (only) around the edges because of mass diffusion).*

Experimental set-up

We developed a set of transparent, cylindrical autoclave cells to visualize glass samples under complex schedules of temperature and pressure. The primary cell—here autoclave A (figure S4A) —was made from aluminum and included a set of viewing windows, as well as dedicated ports for supplying pressure (Fluigent pressure generator) and heat using silicon oil as the thermal fluid (Unistat thermobath). This cell is capable of providing active cooling. A camera was placed overhead to record images using a high magnification objective (105 mm) and illumination was provided from below using an LED light source with a mirror at 45°. The temperature was controlled via a set of PT100 sensors placed directly on the sample at two locations (figure S4B). The edge temperature T1 was used as part of the control loop of the system to regulate the temperature of the silicon oil. The T2 temperature was deemed representative of the target imaging area where we took our bubble measurements. The secondary cell, autoclave B (not shown) was made from stainless steel, heat was provided via a set of heating ropes (no cooling), and the magnification was smaller (75 mm objective). Only the equivalent of temperature T1 was measured (15 mm from the edge). Hence, a calibration was made to match this temperature to the T2 temperature from autoclave A. Finally, we tracked bubbles in three separate regions of interest (ROIs) inside small target imaging area of the sample. The analysis was then performed using ImageJ and python.

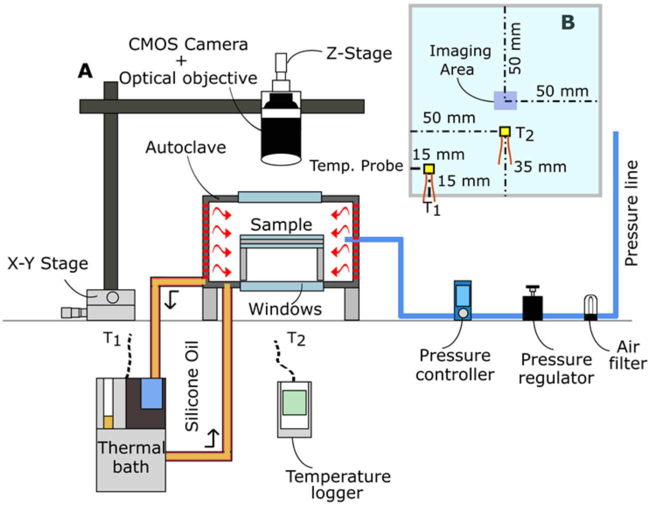


*Figure S4: **A** Transparent autoclave set-up. **B** Glass sample schematics detailing the relevant temperature measurements and the target area whence the bubble images are taken.*

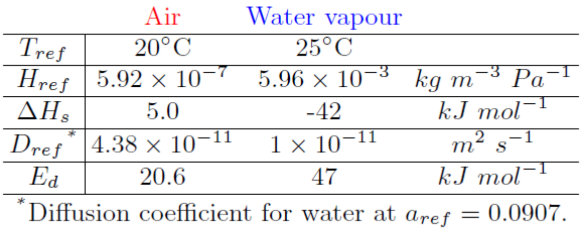
Mass Transport in PVB: air and water

Table S2 presents the physical constants for air and water used in the bake test simulations. Air properties can be found in Arauz-Moreno, Piroird, & Lorenceau (2025). The corresponding ones for water are found in Arauz-Moreno, Piroird, & Lorenceau (2023). Water transport in PVB depends strongly on temperature and moisture. In particular, water has a variable activation energy of diffusion $E_d(T)$, which we simplified here by taking an average value $E_{d,avg}$ from the range of 20-140°C. The diffusion coefficient is likewise moisture dependent. Hence, the Arrhenius expression was taken as

$$\ln\left(\frac{D}{D_{ref}}\right) = -\frac{E_{d,avg}}{R_u}\left(\frac{1}{T}-\frac{1}{T_r}\right) - \gamma\left(a - a_r\right)$$

where $\gamma = -1.4$ and $a_r = 0.0907$.

Table S2: Mass transport constants



	Air	Water vapour	
T_{ref}	20°C	25°C	
H_{ref}	5.92×10^{-7}	5.96×10^{-3}	$kg\ m^{-3}\ Pa^{-1}$
ΔH_s	5.0	-42	$kJ\ mol^{-1}$
$D_{ref}{}^{*}$	4.38×10^{-11}	1×10^{-11}	$m^2\ s^{-1}$
E_d	20.6	47	$kJ\ mol^{-1}$

*Diffusion coefficient for water at $a_{ref} = 0.0907$.

Nucleation in finished glass

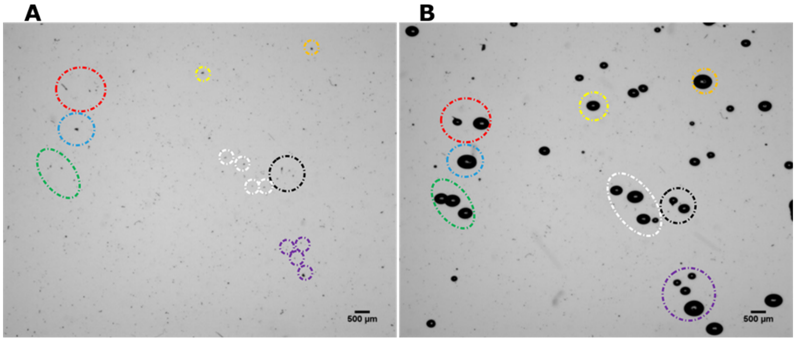


Figure S5: Autoclave images of faulty LSG samples. ***A*** *Before bake testing (16hrs, 100°C).* ***B*** *Post bake testing. The circle areas help identify the location of gas nuclei.*