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Influence of treating parameters on thermomechanical properties of recycled epoxy-acid vitrimers

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A finite-element computational model was used to study the influence of process conditions on the ultimate strength of welded samples. Following the previous work [1], the model captures the stress relaxation of vitrimer particles and their interfacial welding during the reprocessing.

Stress relaxation of bulk materials

The stress relaxation behavior is described using an exponential function:

$$\sigma = \sigma_0 \exp\left(-\frac{t}{\tau}\right), \tag{1}$$

where σ_0 is the initial stress before relaxation. The relaxation time $\tau \approx k^{-1} exp(E_a/RT)$ with k being a kinetic coefficient, T being the Kelvin temperature, R being the gas constant, and E_a being the activation energy. In the previous works [2, 3], the model parameters were determined by performing a group of stress relaxation tests on vitrimers at different temperatures.

Interfacial welding kinetics

During the surface welding, polymer chains diffuse onto the interface and connect *via* covalent bonding. The interfacial fracture energy (i.e., the welding strength) is proportional to the interfacial chain density. In the previous work by Yu et al. [2], a lattice model was used to study the interfacial welding of vitrimer CANs. The evolution of interfacial chain density follows:

$$n_f(t) = n_0 + \sum_{i=1} \beta_i \exp\left(-\frac{t}{\alpha_i}\right), \tag{2a}$$

with

$$\alpha_i = \left(\frac{2N}{2i-1}\right)^2 \frac{3\tau}{2\pi^2},\ \beta_i = -\frac{4n_0}{(2i-1)\pi} \sin\left(\frac{2i-1}{2N}\pi\right). \tag{2b}$$

In above equation, n_0 is the chain density of bulk CAN, N is the number of lattice in the vertical direction of interface, τ is the relaxation time of CANs given in Eq. 1. Detailed parameters are listed in the previous work [2] on the same materials.

Finite element computational simulations

During the finite element simulations, the stress relaxation behavior is realized by defining viscoelastic properties of materials *via* Prony series. For the interfacial behavior, a UINTER was defined based on the cohesive zone modeling approach. The force-displacement relation of interface is characterized by using the following linear traction separation law.

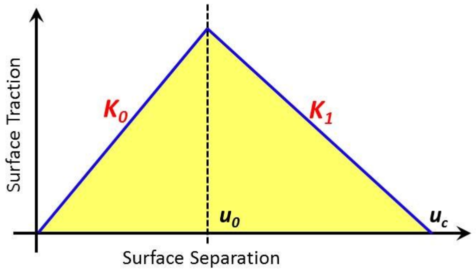


Figure 1. Schematic view of the linear traction separation law

When the interfacial displacement is smaller than the damage initiation displacement u_0, the interfacial stiffness is written as:

$$K_0 = n_f m_c k_f , \tag{3}$$

where n_f is the interfacial chain density in Eq. 2, m_c is the area chain density of polymer, which is a constant, and k_f is the stiffness of single polymer chain before damage. $k_f = 3k_b T / N_k b_k^2$, with N_k and b_k being the Kuhn segment number and Kuhn length respectively. For the cohesive zone model, the damage initial displacement $u_0 = n_k b_k$, which suggests that after the interfacial chains are fully stretched, further stretching them will induce damage.

When the interfacial displacement is greater than the damage initiation displacement u_0, but is smaller than the damage termination displacement u_c, damage is initiated and the damage factor is written as [4]:

$$D = \frac{u_c (u_{\max} - u_0)}{u_{\max} (u_c - u_0)} . \tag{4}$$

u_{max} is the maximum separation in the loading history u_c. If the current separation is greater than u_{max}, then $u_{max} = u$, and the interfacial stiffness is written as:

$$K_1 = (1 - D) K_0 u . \tag{5}$$

The damage termination displacement u_c is determined by the interfacial fracture energy:

$$G = \frac{1}{2} K_0 u_0 u_c . \tag{6}$$

Finally, the surface traction is projected into the normal and shear direction of interface according to the relative displacement to obtain the interfacial normal and shear stresses.

The vitrimer particles are shown to exhibit non-regular shape and size distribution, which are challenging to model during the finite element simulations. In this preliminary work, we make a simple assumption that the particles are all spherical balls with the same size, and they are tightly packed as shown in the following figure. In this manner, a representative model can be used to simply the problem. While this is not a perfect approach to study the vitrimer reprocessing, it can provide valuable insights to the influences of some process parameters, such as the treatment temperature, time, and pressure.

During the 2D plane-strain FEM simulation, the representative element is first compressed by a constant pressure at a given temperature and followed by isothermal stabilization, wherein the particles are gradually squeezed together due to the BER-induced creep, and the interface is welded. After being heated for a given time, the external pressure is removed and the temperature is reduced back into the room temperature. In the final step, the welded representative element is stretched at 10%/min until break.

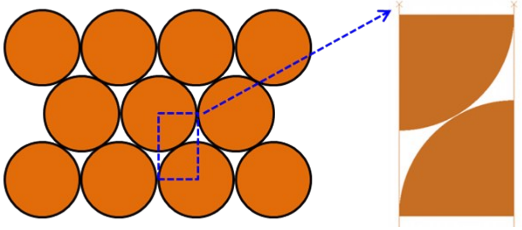


Figure 2. A representative model based on the assumption that the particles are identical spherical balls.

Results and Discussions

Fig. 3 also shows the Mises stress distribution within the FEA model at different states of reprocessing, wherein the welding pressure is 3MPa, and the welding time is 60min at 160^{o}C. It can be seen that during the isothermal stabilization, the particles gradually contact to close the voids, and the internal stress distribution tends to be uniform. After unloading, there is essentially no residual stress and internal voids within the welded structure. During the final stretch, the interfacial crack starts at the top corner and propagates until complete separate of the particles. The ultimate strength and stretch ability of reprocessed samples depend on the interfacial fracture energy among particles.

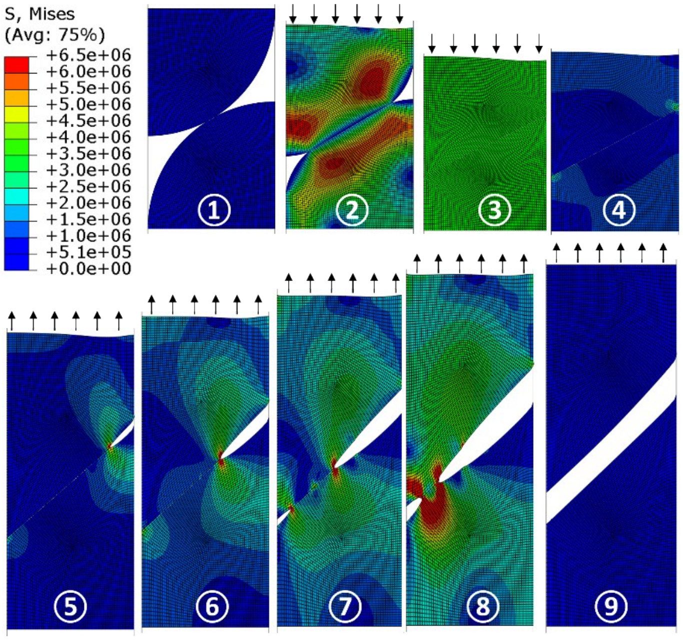
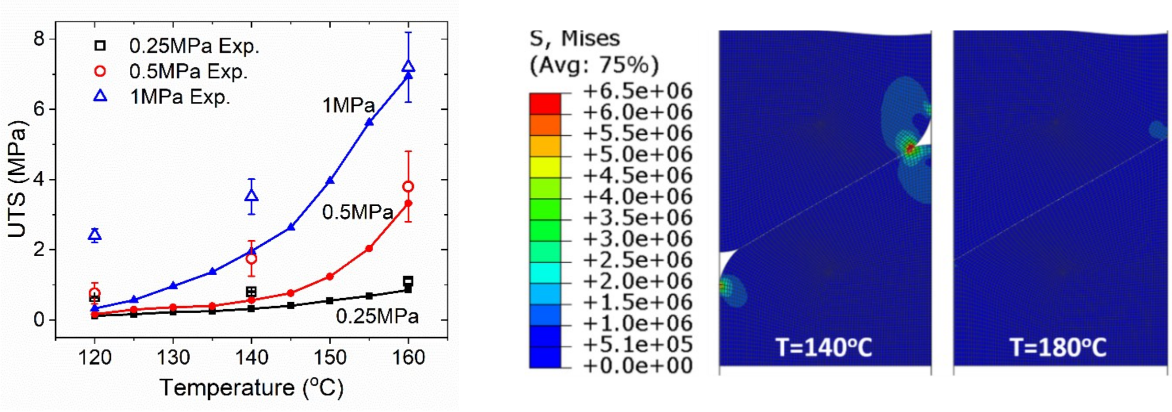


Figure 3. Mises stress distribution within the FEA model at different states of reprocessing. 1: Initial state; 2: Compression; 3: Isothermal Stabilization; 4: Unloading; 5-9: Stretching with interfacial fracture

Fig. 4a shows the ultimate strength of reprocessed samples in both experiments and simulation, wherein the particle size is 178 *um* (*i.e.,* the average size of the small particles). It is seen that the ultimate strength increases with welding pressure and temperature. The reason can be revealed by looking at the stress state after unloading (Fig. 4b). With a low treatment temperature or pressure, the particles cannot fully contact after stabilization. Significant residual stress develops at the tip of interface, with the central part of interface being compressed, and the interface boundary being stretched to balance the central compressive stresses. For example, when the welding temperature is 140^{o}C, the residual stress is up to ~6MPa, while at 180^{o}C, the stress is only ~36kPa. Both incomplete welding and residual stress development lead to the welded structure easily break.

On the other hand, the figure tells that when a higher welding pressure or temperature is applied, the experimental and simulation results agree well. But when a smaller welding pressure or temperature is given, the ultimate strength in the simulation is much slower than that in the experiment. This is because the non-regular size and shape of polymer particles will lead to a more compact arrangement in the experiments than the schematic shown in Fig. 2. When a higher pressure or temperature is applied, most voids in the powder sample would be essentially closed during the welding step, and the ultimate strength of reprocessed sample largely depends on the interface strength. However, when a small pressure is applied, the porosity of the reprocessed sample is higher than that in experiments, so a lower strength is predicted.



(a) **(b)**

Figure 4. (a) Ultimate strength of reprocessed sample in both experiments and simulations. **(b)** Stress state after unloading.

It should be noted that the 2D representative FEA model has no size effect. That means, with identical process conditions (e.g., pressure, time, temperature), the particle size has no effect on the predicted stress-state and ultimate strength (Fig. 5). However, the preliminary study provides valuable insights to the reprocessing problem. In addition to the results discussed above, it is hypothesized that with the same pressure, the particle size might not be the dominating parameter to determine the welding efficiency and ultimate strength, but the distribution or particle shape is more important. For example, with a broad distribution, the small particles fill in the gaps among large particles. Detailed influences and modeling strategy deserve future study.

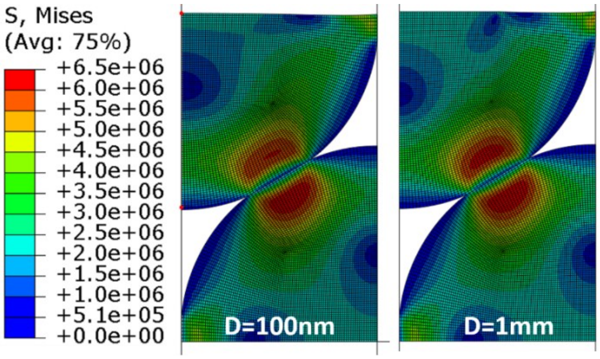


Figure 5. The stress-state of the FEA model with different particle size. The model has identical stress-state, which suggests that the current FEA representative model cannot study the influences of particle size

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