Development of self-healing films to improve durability of VIPs by in-situ remediation of film defects

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ABSTRACT
The integrity of the VIP barrier film or envelope is a critical for maintaining the ultra-low thermal conductivity of VIPs. Here, the concept of a self-healing barrier film is described and demonstrated. The self-healing concept is based on an addition reaction between two chemicals, without the need for any external stimuli. The chemicals are incorporated as coatings in a multi-layered film and are initially kept separate with a partition layer. In case of damage, the chemicals would mix, react and heal the damage. Tests of small-scale film samples in a custom vacuum pump apparatus by puncturing the samples demonstrated the proof-of-concept. The tests indicated that the chemicals reacted and healed the puncture immediately to maintain the system vacuum. The intact and punctured self-healing films showed near-identical behaviour, while a control sample allowed the pressure to rise to atmospheric levels on puncturing.

Development of films with coated chemicals using tape casting and slot die coating methods is also described. These are low-cost and mature technologies, which are commonly used by various industries. The proposed chemicals are low-cost, commercially available materials. Thus, the self-healing technology is expected to be inexpensive and scalable.

KEYWORDS: self-healing film, multi-layered barrier film, roll-to-roll manufacturing, durability of VIPs

INTRODUCTION
Self-healing strategies can be classified as intrinsic (one-part chemistry) and extrinsic (two-part chemistry) mechanisms [1]. One-part healing chemistry, based on reversible covalent bond or supramolecular chemistry, typically requires external stimuli, such as light or heat, which may not be applicable for VIPs in building applications (usually VIPs are covered by multiple layers of materials). Extrinsic self-healing occurs with the help of a healing agent and catalyst. The present work evaluated a vacuum assisted, two-part addition reaction as the self-healing process for barrier films of vacuum insulation panels (VIPs). Addition reaction involves short reaction time, which are desired so that the films can heal themselves from damage before the VIPs lose their internal vacuum.

In this study, reaction kinetics were investigated with multiple combinations of chemicals to identify the most promising pair of epoxy and curing agent for subsequent proof-of-concept testing. Small-scale coated film samples with the self-healing chemicals were produced and tested in a vacuum pump apparatus. The self-healing film samples were punctured and the ability of the healed film samples to maintain the system vacuum was observed using a pressure gauge. Further, scalable roll-to-roll (R2R) manufacturing trials were performed to create multi-layered coated films in a continuous process.

MATERIALS

Fig. 1 shows the schematic of the multi-layered self-healing film [2]. We started our investigations of chemicals for reaction kinetics and suitability as coating agents. The team discussed different film materials that are commercially available and started experimenting with polyethylene terephthalate (PET), polyethylene (PE) and co-extruded polymer films. PET and metallized-PET (mPET) films are currently used for barrier films of VIPs. Based on available information, the oxygen transmission rates of PET and mPET films are in the ranges 31-93 and 0.16-1.7 cc/m^2/day.[1] For reference, the OTRs of typical VIP barrier films are 0.07-0.0005 cm^3/m^2/day. The multi-layered films with the self-healing chemicals and nanoclay additive are expected to achieve similar OTRs as VIP barrier films [2].

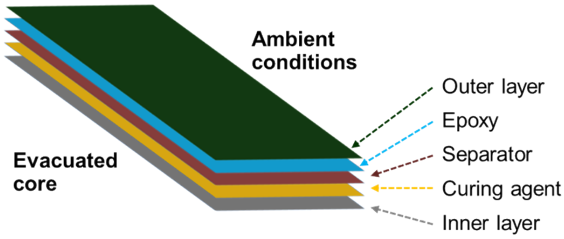

Fig. 1. Schematic of self-healing film.

An addition reaction with epoxy and curing agent (CA) resulted in a fast healing reaction. A commercial epoxy, EPON 8111[2], and polyethyleneimine (PEI)-based curing agents (PEI-10K and PEI 800) are used; 10K and 800 refer to the molecular weights of the chemicals. The chemicals were mixed with a nanoclay (NC) for viscosity control and processability. Fig. 2 shows the measured viscosities of different slurries at different shear rates. Development of shear thinning slurries at typical R2R coating shear rates (100-1000 s-1) is critical for good coating quality and all slurries exhibited viscosities in the current range. Initial coating trials were done with small-scale tape caster with different slurries and substrates. Fig. 3 shows the tape casting method and some sample coatings. The coatings were observed to retain their shape even when held vertically.

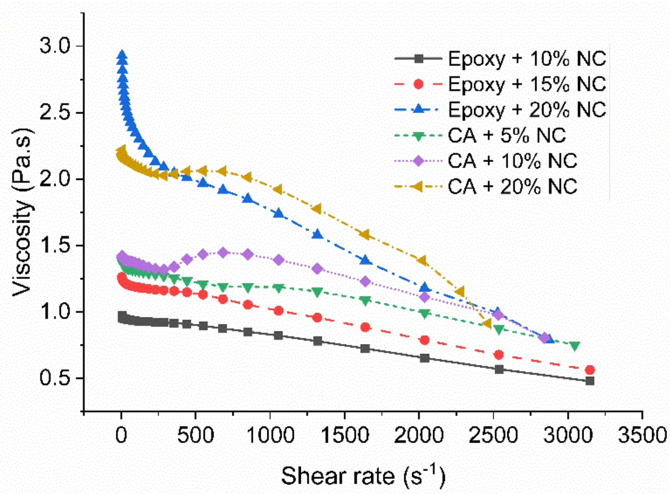

Fig. 2. Measured viscosities of slurries.

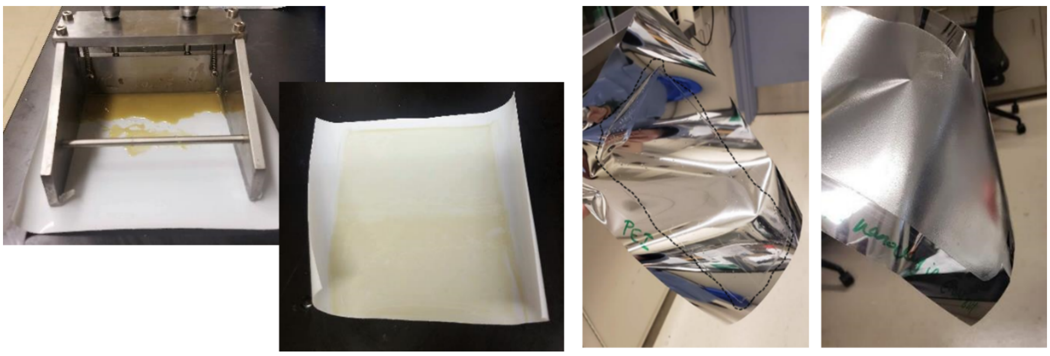

Fig. 3. Left: Tape casting method; Right: Sample coatings.

[1] http://www.polyprint.com/flexographic-otr.htm
[2] http://www.hexion.com/en-us/brand/epon

SELF-HEALING EXPERIMENTS

Hand-assembled self-healing samples were tested via puncture experiments in a custom vacuum apparatus, see fig. 4. The apparatus consists of the sample holder that exposes the film samples to the atmosphere on one side and a partial vacuum on the other. The sample holder is connected to a vacuum pump and a pressure gauge via tubes; the vacuum is held within the tubes.

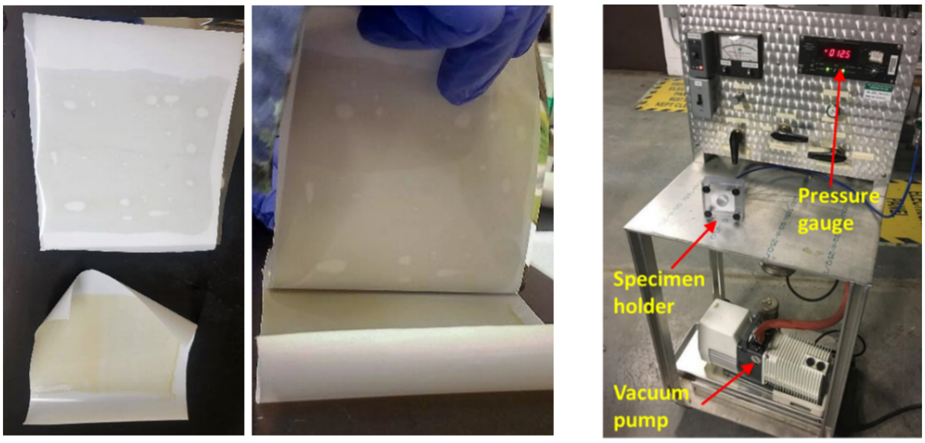

Fig. 4. Left: Hand-assembled self-healing film samples; Right: Custom vacuum apparatus.

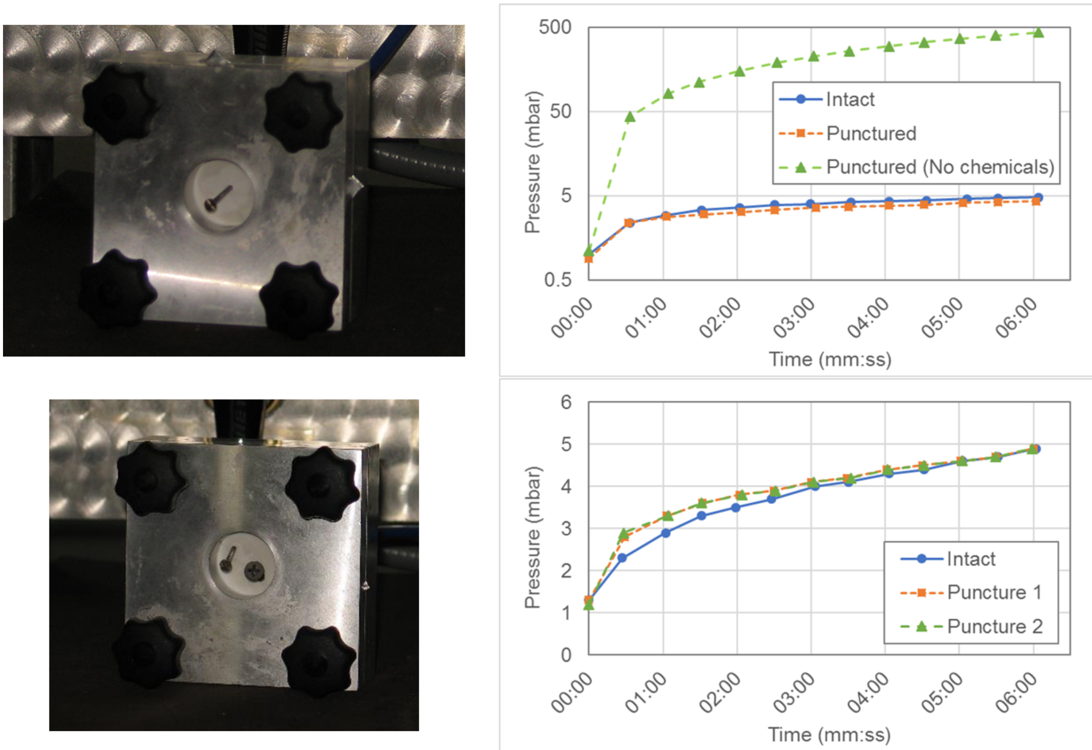

Fig. 5. Left: Punctured self-healing film samples; Right: Pressure increase with time.

For testing, the film samples were installed in the sample holder. Next, the vacuum pump was turned on to evacuate the system to 1 mbar. The pump was then turned off and the pressure was monitored for several minutes with the test sample remaining intact to gather the baseline pressure data. Next, the vacuum pump was turned on again to re-evacuate the system to 1 mbar and then turned off and the test sample was punctured. The system pressure was again monitored and recorded for several minutes or till the system pressure rose to the atmospheric pressure. Samples with and without the self-healing chemicals were tested. Fig. 5 shows samples that were punctured with a needle and a screw and the resulting pressure increase. The results showed that, with self-healing chemicals, the punctured films maintained the low system pressure similar to intact films. It is noted that the system is not hermetically sealed, so there is some pressure increase due to air leakages even with the intact films. Without the self-healing chemicals, the system pressure rose quickly when the films were punctured.

R2R TRIALS

Finally, the team has started performing trials to create self-healing films in an industry-scalable manner using a slot die coating machine. Fig. 6 shows one of the coating trials to create multi-layered film with interleafed substrates and coatings. In this scenario both epoxy and curing agent coatings were applied to the opposing surfaces of the separator layer (see fig. 1). The inner and outer layers are interleafed sequentially to create the overall multi-layered structure.

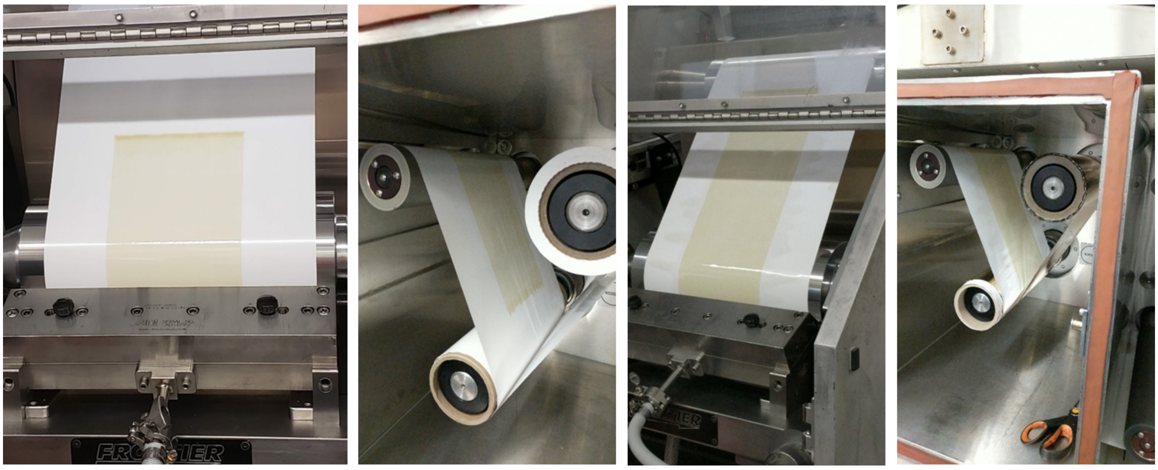

Fig. 6. Multi-layered slot die coating trial. From left-to-right: (i) first layer on coating on first substrate (which becomes the separator layer shown in fig. 1), (ii) an interleafed layer (which becomes the inner layer), (iii) second coating on the exposed face of the separator layer, and (iv) final interleafed outer layer.

CONCLUSIONS AND FUTURE WORK

The current work showed the ability of prototype self-healing films to heal quickly and maintain the film impermeability, evidenced by puncture tests in a custom vacuum apparatus. Some preliminary trials were performed to created multi-layered, coated films using a continuous roll-to-roll manufacturing process.

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