Understanding and Controlling Chemical Transport in Coatings

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Polymer-Agent Interactions

- Polymeric materials are used on military and emergency response assets, including the exteriors of vehicles and support equipment, and exhibit different toxic chemical absorption and retention behavior due to variations in mechanical properties and chemical composition. For materials like protective coatings, there are knowledge gaps in how to design polymer binders that are tuned for chemical resistance that can additionally incorporate solids to form composites appropriately
- Past work on contamination of polymer-based coatings by liquid contaminants has shown there are routes for redistribution and localization of chemical concentration via surface wetting, capillary uptake, as well as diffusive transport into bulk layers

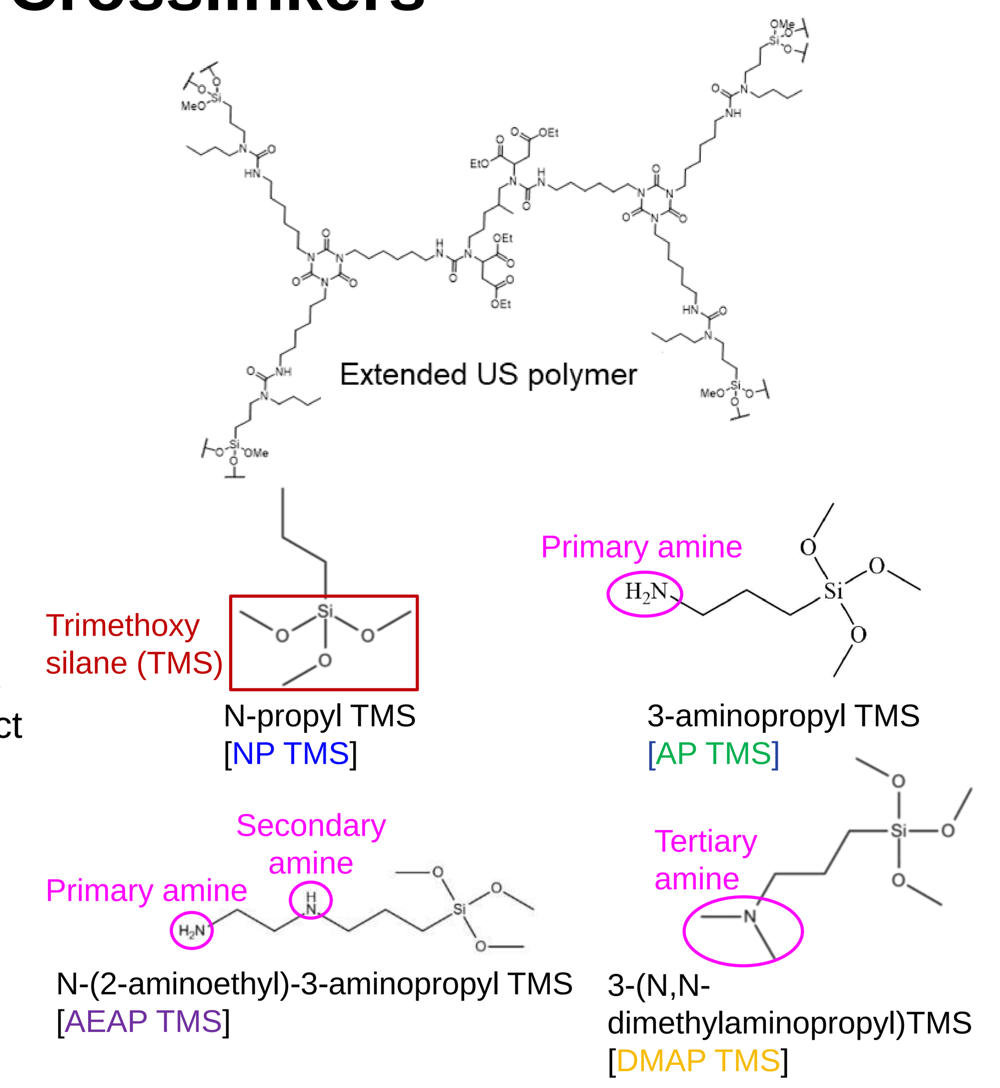
Factors that influence the types of chemical transport and degree of chemical retention for polymeric coatings:

- Specific polymer binder chemical structure and mechanical properties [solubility and transport rates]
- Solids supported in polymer binder matrices, e.g., pigment particles, matting agents [permeation]
- Physicochemical interactions between agents and coatings chemical and morphological/defect structure [surface adhesion]

Overall goal: resolve what chemical interactions and materials properties are important to control and tune for the purpose of guiding formulation development for engineered coatings

Polysiloxane Binder with Crosslinkers

- Organosilane polymers (i.e., urea silane (US)) used in sol-gel/polysiloxane networks were studied to determine relationships between mechanical properties and chemical resistance
- A pseudo-homomorphic series of silane crosslinking additives with variable amine functional groups were used to determine the relationship between polymer network structure and chemical absorption
- Network thin film mechanical properties as a function of crosslinker type and loading were determined using dynamic mechanical analysis (DMA)
- Chemical retention for multiple probe molecules was characterized for these polymers, and select additives demonstrated a reduction in chemical retention



Polysiloxane binder with 4 additives tested at loadings of 1, 5, 10, 20% (mass additive / mass polymer)

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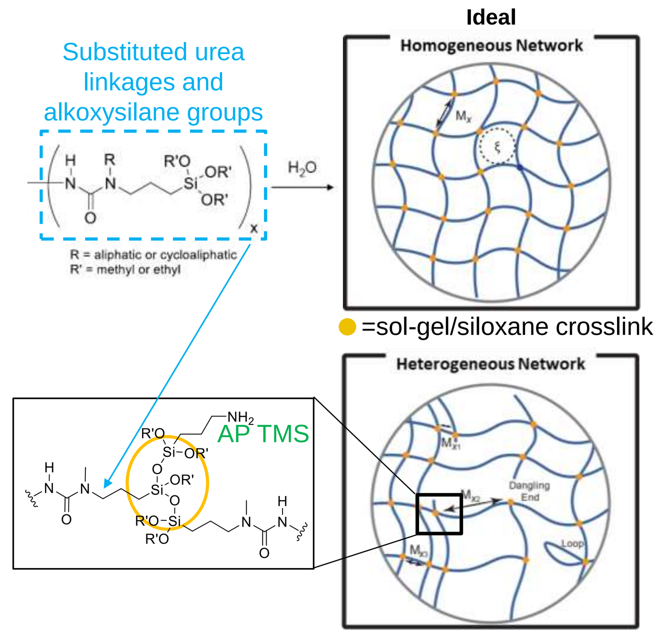
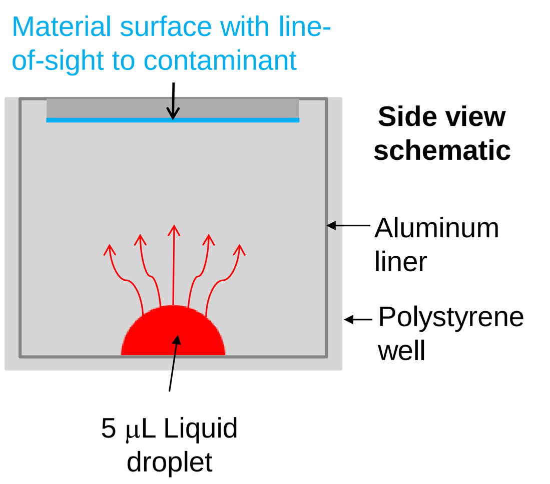
Materials Preparation

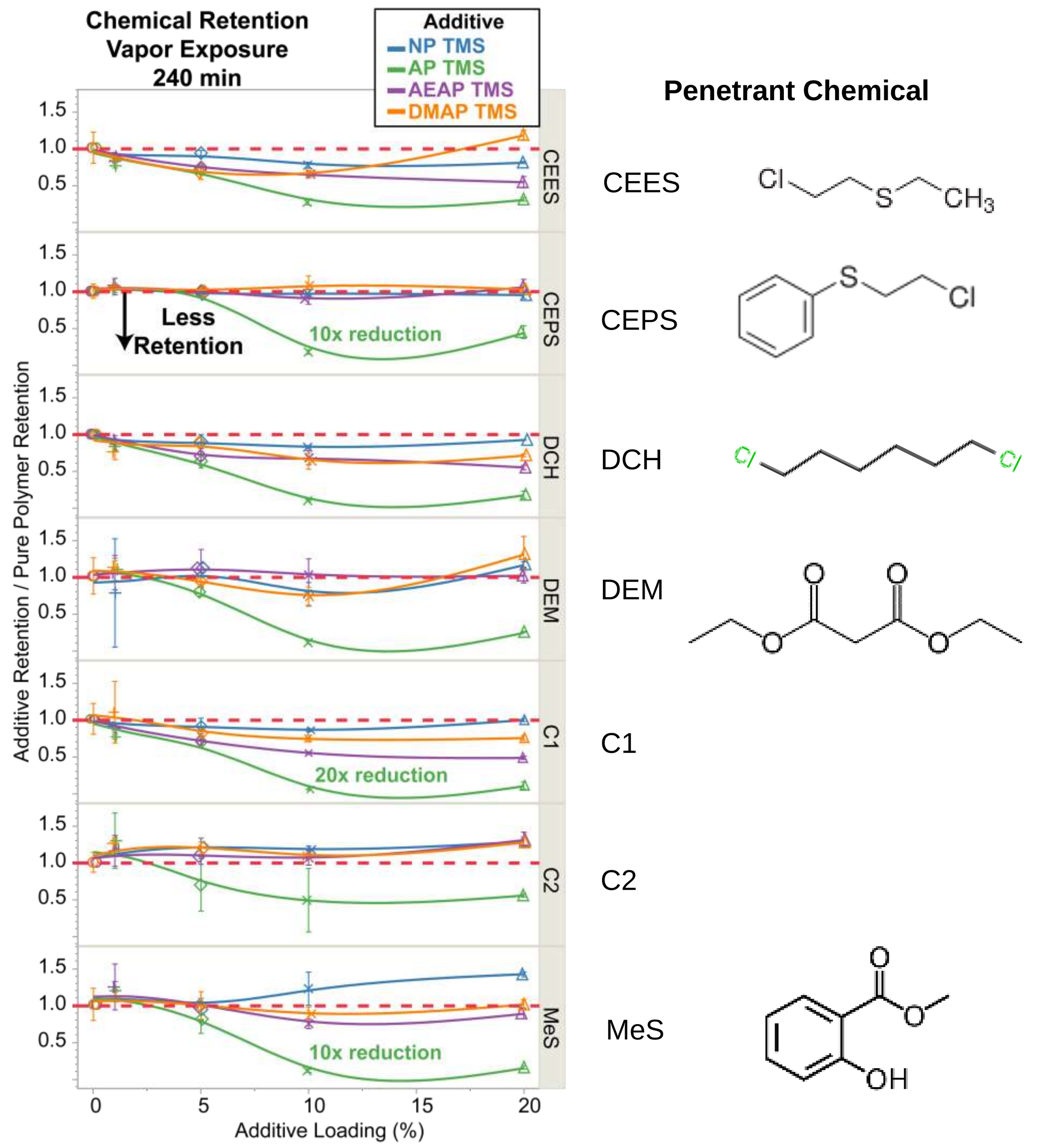
- Organosilanes form sol-gel networks, which offer excellent hardness and hydrocarbon resistance
- US structure can be synthesized with varying mechanical properties (non-extended vs extended polymer backbone structures)
- Polymer synthesis permits detailed investigations on agent retention as a function of material mechanical and chemical properties
- Samples were sprayed on primed, metal substrates for retention measurements or release paper for DMA measurements to produce ~30 µm thick films



Retention Via Vapor Contamination

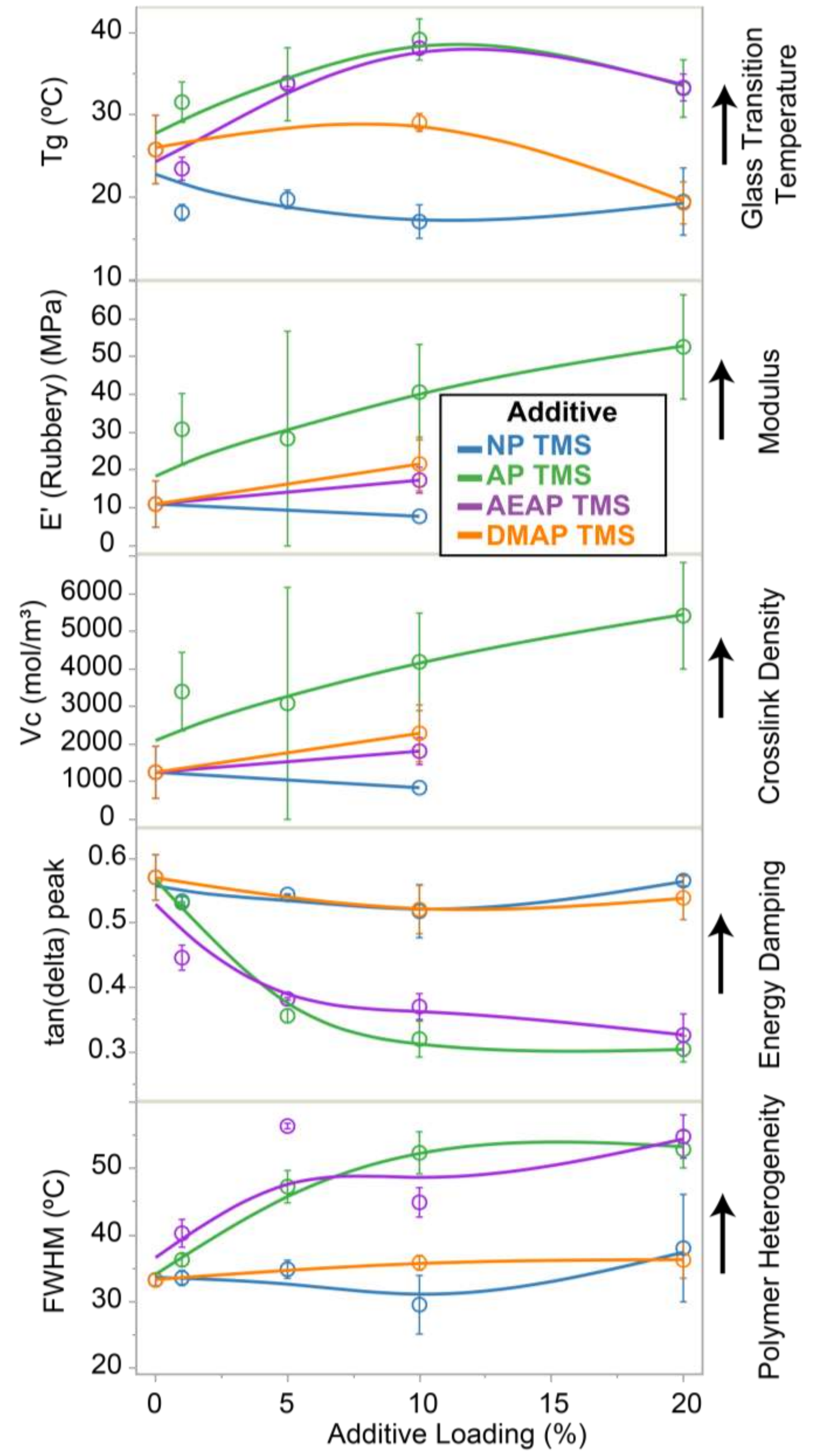
- Traditional chemical resistance measurements use liquid exposure and treatment processes to remove the bulk liquid, but retention signal can be dominated by liquid adhesion to the polymer surface
- New vapor exposure technique developed to eliminate the contribution of surface adhesion to the retention measurement and the need for a treatment process
- Sprayed polymer films exposed to vapor from a proximal droplet in a sealed volume for 240 min, then extracted
- Multiple penetrant chemicals used to identify how retention is influenced by the chemical structure of the contaminant





- Normalized retention (Retention with Additive / Retention for pure polymer) quantifies how the additives influenced chemical retention
  - Substantial reduction (~10x) in retention for all chemicals in polymer with 10% AP TMS loading (except C2 with ~2x reduction)
  - Only minor differences across penetrant chemicals
- Chemical retention is a dynamic process that can may occur over hours to days
- Intermediate duration exposures may not have achieved equilibrium and the results indicate a *transport rate* limited response
- A long duration vapor exposure (18.5 h) for the 10% AP TMS loading exhibited no difference from the polymer without the additive
- Future experiments will consider time-resolved mass uptake to monitor transport rate and solubility effects

Polymer Mechanical Properties



- Dynamic Mechanical Analysis (DMA) was used to characterize polymer mechanical properties that reveal information about polymer structure
- The polymers tested here had a glass transition temperature, T_g, slightly above ambient laboratory conditions, most samples were below the T_g for chemical retention testing
- Higher crosslink density increases the storage modulus (E'), and decreases the mesh size which tend to slow the transport of penetrants in the polymer
- Polymer heterogeneity, indicated by the full width at half maximum (FWHM) of the tan δ peak, can result in various mesh sizes and create tortuous paths that may decrease the apparent diffusivity of penetrants in the polymers
- In some cases, the additive loading resulted in brittle films that failed during testing

Effect of Additives

- Many mechanical similarities exist between polymer films with AP TMS and AEAP TMS – both additives have primary amines
- Inclusion of AP TMS and AEAP TMS produces higher glass transition temperature and influences polymer heterogeneity
- AP TMS has most significant influence on crosslink density
- Only AP TMS shows a significant reduction in chemical retention across the probe molecules chosen
- Change in agent retention may be related to mechanical (e.g., crosslink density) and other polymer network characteristics

Conclusions

- A vapor exposure method was developed to characterize chemical retention in polymers
- Multiple crosslink additives were evaluated at different loadings in an extended polysiloxane binder
- Additives with primary amines were found to influence polymer mechanical characteristics, but only AP TMS influenced agent retention results
- DMA data indicated that AP TMS most significantly influenced crosslink density
- Comparison of chemical retention for vapor exposure of short (4 h) vs. long (18.5 h) durations indicated that AP TMS may influence the sorption (transport) rate, but not the equilibrium solubility – consistent with a change in crosslink density
- Similar tests conducted with the inclusion of solids show that, for this polymer system, altering the binder properties has more influence on contaminant retention
- These data show that understanding the factors that influence contaminant transport in the binder are critical towards understanding how to formulate polymers for improved chemical resistance

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