

CONTROL OF MOISTURE AND VOLATILE ORGANIC COMPOUNDS BY SORBENT-LOADED COMPOSITES

S.E. Solovyov,¹ T.H. Powers,¹ S.A. Incorvia,¹ J.A. Williams,² P.E. Koch²

¹ Multisorb Technologies, Inc., 325 Harlem Road, Buffalo, NY 14224, USA

² Pennsylvania State University, The Behrend College, Erie, PA 16563, USA

Abstract

The integrity, performance and service time of certain automotive subsystems is adversely affected by moisture ingress into contained environments. Corrosion of air conditioning (AC) system components caused by moisture initially present in the refrigerant and moisture permeated through the seals during the AC unit service life is one example. Another one is water vapor condensation in optical components used for night and rear vision systems as well as optical proximity sensors, often causing their malfunction in changing environmental temperature and humidity conditions. Desiccating multiforms attached to a condenser coil have long been used in automotive AC units to absorb the residual moisture and the moisture permeating from outside. The new direction in AC moisture control is the use of sorbent-loaded polymer composites in AC structural parts that eliminate the need for individual desiccating multiforms, their assembly operation as well as the associated noise from the assembly. Desiccating composite enclosures and seal materials are simultaneously targeted for improving performance of optical components. Volatile organic compound (VOC) emissions from fuel tanks and lines into atmosphere can also be reduced by using VOC absorbing composite materials as reactive barriers to permeation in fuel tank and supply line design.

The performance of sorbent-loaded composites is evaluated from the standpoint of two distinct design targets: removal the target vapor from the contained environment and reducing the rate of ingress from the external environment. The concepts of the layer reactivity, the adsorptive capacity, and the sorption rate are applied to the homogeneously reactive media and the sorbent-loaded polymer composites. The corresponding differences in performance and design requirements are discussed.

Background

Sorbent-loaded composite materials are a part of a broader class of active packaging materials designed for dynamic control of contained environments. In the simplest example, a thermoplastic polymer is melt-compounded with an inorganic sorbent particulate with a possible addition of surfactants, dispersion aids and compatibilizing agents to control the composite morphology and particle dispersion. When the design goal is to separate two distinct environments and to prevent the diffusive mass exchange between them, such materials are made into a film or sheet type barrier structure and are called *reactive barrier composites* (RBC). When the goal is to reduce gas or vapor amounts within the contained environment through accelerated sorption into the enclosure made from the active material, a large loading fraction of the active component into a composite is usually required. Such highly loaded composite materials are often referred to as *resin-bonded sorbents* (RBS). What makes RBS different from RBC is the requirement of high rates of vapor sorption into the composite. Low sorption rates do not allow to utilize the adsorbing capacity of the active component in RBS efficiently. On the other hand, low sorption rates in RBC are beneficial because they enhance the RBC transient barrier performance and delay the depletion of RBC adsorptive capacity. In

order to increase the sorption rates, RBS materials should possess a high permeability to target gas or vapor so that it could be rapidly delivered to the dispersed sorbent. One way of achieving that is to produce highly permeable contiguous polymeric matrices loaded with the sorbent particles (Fig. 1). An alternative way is to create highly porous composite morphologies by using standard automotive structural resins as matrices, in the same time ensuring that all sorbent particulate is bonded to the matrix and the particle dust is eliminated (Fig. 2). Simultaneously achieving the complete sorbent bonding, maintaining the required mechanical properties of a highly porous composite, and providing the required adsorptive capacity and sorbent loading within the limited part volume may not be easily attained. Therefore we initially focus on solid non-porous RBS and RBC as substrates for performance analysis.

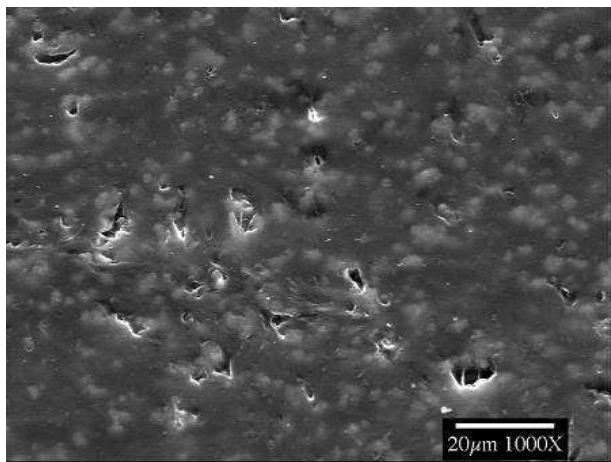


Figure 1: 40 wt.% molecular sieve in polypropylene.

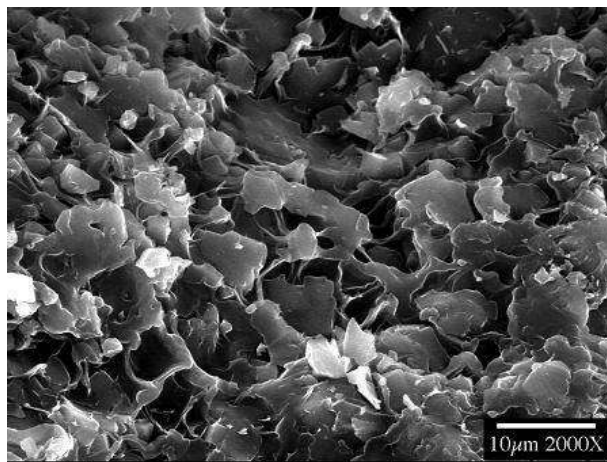


Figure 2: 40 wt.% molecular sieve in nylon.

Reversible and irreversible absorbers are two distinct classes of sorbent additives that can be used in RBS and RBC. Irreversible absorbers such as calcium oxide (for water vapor) and reduced transition metals (for oxygen) utilize chemical reactions of the additive with the target solute, which are irreversible at the conditions of use and are often stoichiometric. Catalytic reactions can be also used to irreversibly convert the solute such as ethylene gas into other (neutral) compounds. Irreversible absorbers are referred to as *scavengers* of a specific solute. Reversible absorbers such as silica gel and synthetic molecular sieves (common desiccants) can freely absorb and desorb moisture, while the equilibrium absorbed water amount depends on the relative humidity (RH) in the surrounding environment. The full theoretical adsorption capacity of such reversible absorbers may not be attained unless an excessively high RH is present in the environment. As the first step of analysis we investigate irreversible absorbers and the corresponding performance of RBS as reactive barriers to permeation and RBC as reactive media for vapor removal from the contained environment.

Reactivity Analysis

Both non-porous RBC and RBS cannot function efficiently unless their reactivity is sufficiently high. For purposes of this discussion the term “reactivity” will refer to the effective reaction rates of irreversible chemical scavengers and the forward (sorption) rates of reversible

physical absorbers with the solute. The rate of solute “reaction” with the sorbent is controlled not only by the inherent sorption properties of the sorbent particles but also by the rate of solute diffusion to the adsorbing sites and the probability of collision with such sites. A simplified overall mechanism of many common bimolecular irreversible stoichiometric isothermal scavenging reactions of the permeating solute C with the scavenging reactive sites R immobilized within a polymer matrix can be described as¹:



with the common second order expression for the reaction rate :

$$r = K[R][C] \quad (2)$$

and the stoichiometric coefficient of the non-catalytic reaction. In case of catalytic reactions the solute scavenger is not consumed during the course of the reaction. For reversible absorbers the rate refers to the forward reaction rate and the stoichiometric coefficient refers to the effective “saturation” capacity of the sorbent in equilibrium with the external solute pressure or RH, i.e. for desiccants the maximal local utilized capacity (RH) is a function of local RH in the surrounding matrix. The one-dimensional mass balance of the solute C and the absorber R in the non-catalytic reactive layer with the uniform thickness L and the concentration-independent solute diffusivity D in it is given by:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - KRC = D \frac{\partial^2 C}{\partial x^2} - kC \quad (3)$$

$$\frac{\partial R}{\partial t} = -KRC \quad (4)$$

with the appropriate initial and boundary conditions. The time- and position-dependent pseudo-first-order rate constant k in (3) is defined as:

$$k = k(x,t) = KR(x,t), \quad (5)$$

and the *initial reaction rate constant* k_0 is:

$$k_0 = KR_0 \quad (6)$$

where $R_0 = \text{const}$ is the initial concentration of the activated absorber “homogeneously” distributed in the matrix.

The simplified approach to reactivity characterization of both catalytic and stoichiometric RBC can be divided into two parts: 1) determining the initial pseudo-first-order reaction rate constant k_0 for unbiased diffusion of gas molecules in an infinite matrix volume with the gas diffusivity D in it, “homogeneously” filled with infinitely diluted uniform spherical reactive particles with the diameter d , 2) characterizing the barrier improvement of the uniform membrane made from such material due to reaction. For RBS the second task is replaced by characterizing the rate of sorption into the reactive layer. The first task can be solved using the two-scale coarse-graining approach described below. The second part of the reactive barrier characterization

consists simply of evaluating the initial Thiele modulus ϕ_0 of the equivalent homogeneously reactive RBC with the thickness L :

$$\phi_0 = \sqrt{Da^{II}} = L\sqrt{\frac{k_0}{D}} \quad (7)$$

where Da^{II} is the second Damköhler number, representing the ratio of the characteristic time of reaction to that of solute diffusion in the layer.

The steady-state solute concentration profile across the catalytic reactive layer thickness x/L has the form (Fig. 3):

$$C(x) = C_{in} \cosh\left(\frac{x}{L}\right) + C_{out} \operatorname{csch}\left(\frac{x}{L}\right) - C_{in} \coth\left(\frac{x}{L}\right) \sinh\left(\frac{x}{L}\right) \quad (8)$$

where C_{in} and C_{out} are the fixed solute concentrations within the downstream and upstream layer boundaries, respectively. For thick reactive layers with large reactive capacity we are often justified to use the fixed downstream boundary condition $C_{in} = 0$ corresponding to negligible solute concentration downstream. For simplicity, the cases with $C_{in} = 0$ will not be considered further.

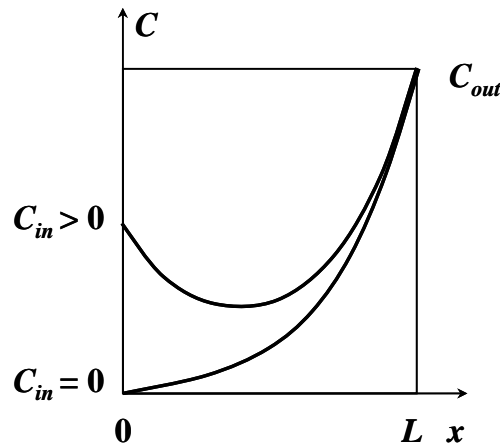


Figure 3: Steady-state solute concentration profiles in RBC and RBS.

The effective solute flux $J_0(t)$ or the solute flux across the unit area of the downstream RBC layer boundary $x = 0$ is obtained by applying Fick's first law of diffusion to the steady-state solution (8) for catalytic reaction:

$$J_0 = D \left. \frac{dC(x,t)}{dx} \right|_{x=0} = \frac{DC_{out}}{L} \operatorname{csch}\left(\frac{x}{L}\right) \quad (9)$$

Respectively, the rate of sorption into an RBS layer is obtained at the upstream layer boundary $x = L$ as (Fig. 4):

$$J_L = D \frac{dC(x,t)}{dx} \Big|_{x=L} = \frac{DC_{out}}{L} \coth(\lambda) \quad (10)$$

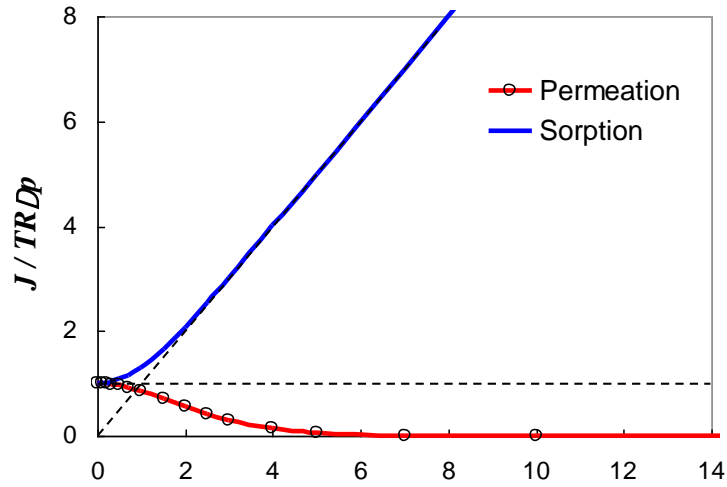


Figure 4: Steady-state rates of sorption and permeation in RBS and RBC layers.

Figure 4 demonstrates the linear dependence of normalized sorption flux in RBS on the layer reactivity λ for $\lambda > 2$. The rate of permeation through RBC on the other hand is the exponentially vanishing function of λ . The corresponding initial barrier improvement factor ϕ_0 due to reaction in RBC is found as a ratio of the effective solute fluxes J_0 through the otherwise identical passive (J^P) and activated reactive ($J_0^R(0)$) barrier layers [1]:

$$\phi_0(P/R) = \frac{J^P}{J_0^R(0)} = \frac{\sinh(\lambda_0)}{\lambda_0} \quad (11)$$

The overall reaction rate in a composite barrier can be either diffusion- or activation-controlled. Activation-controlled systems with $\lambda_0 > 1$ and respectively slow reactions have been shown to result in negligible barrier improvement versus non-reactive barriers [1]. Diffusion-controlled reactive systems with $\lambda_0 < 1$ correspond to the fast reaction limit and produce the desired large barrier improvement until the reactive capacity of the barrier is completely depleted. Note that the barrier reactivity λ_0 is different from its reactive capacity to remove the solute. The reactive capacity of catalytic reactive barriers is infinite by definition, while for non-catalytic barriers it is determined by the stoichiometry of the reaction or equilibrium adsorptive capacity of physical absorbers.

Effects of Reactive Layer Heterogeneity

As discussed in [2] and [3], the rate of gas-solid reactions in a polymer composite depends on the gas diffusivity in the polymer matrix, the mean particle size of the reactive additive, the volumetric loading of the reactive additive, the inherent reactivity of the reactive additive, and the particle morphology and porosity (providing an access to reactive sites). Fig. 5 represents the general structure of such composites and the gas molecule diffusive paths in the matrix resulting in either their adsorption or permeation across the layer.

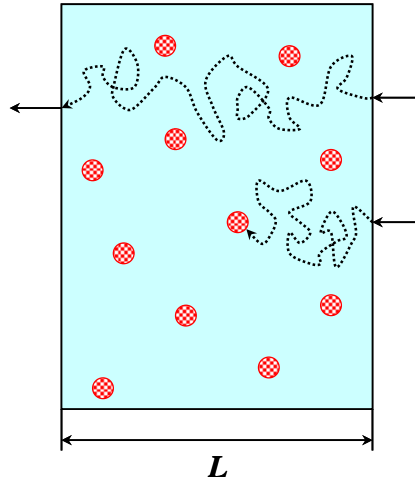


Figure 5: General structure of RBC/RBS composites.

For highly filled RBS composites the effects of heterogeneous distribution of the reactive sites are of lesser importance while a high overall equilibrium adsorptive capacity of a composite obtained through the increased sorbent loading is critical for its sorption performance. For RBC composites that are often diluted, the low probability of molecular collisions with the particles can reduce the barrier reactivity and respectively its barrier performance. The pseudo-first-order rate constant k_0 in (6) can be estimated using the coarse-grained unit cell and large scale (overall barrier thickness) approaches [2]. The unit cell is defined as a unique volume of the composite solely associated with the specific particle, and such unit cells comprise the entire layer. By taking the length of unit diffusive displacement of gas molecule equal to the mean particle diameter d , the following rate constant estimates were obtained:

$$\text{Unit cell: } k_0 = 3.898 \frac{D}{d^2} (\rho_p)^{\frac{4}{3}} p_R \quad (12)$$

$$\text{Large scale: } k_0 = \frac{D}{d^2} \rho_p \frac{2d^2}{L^2} p_R \quad (13)$$

where ρ_p is the volume fraction of loaded particulate and p_R is the reaction probability upon gas molecule-to-particle collision. The comparison of these two model predictions is shown in Fig. 6. Both models prove that reducing the mean size of the additive is the preferred way of increasing the barrier reactivity compared to increasing the additive volume fraction. The reason is that the barrier reactivity k_0 is inversely proportional to the mean particle size: $k_0 \sim 1/d$, while

k_0 increases only as a fractional power of p : $k_0 \sim p^{2/3}$ from (12) or $k_0 \sim r_p^{1/2}$ from (13). On the other hand the ultimate reactive capacity of the barrier is proportional to the loaded weight fraction $f_p = p / M$ of the additive. Therefore the improvement in barrier reactivity by particle size reduction should not be compromised by the simultaneous reduction in the loaded volume fraction.

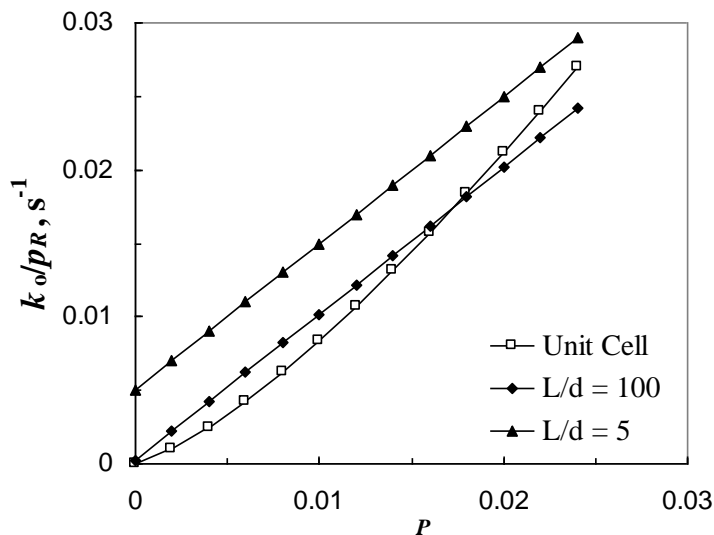


Figure 6: The reaction rate dependence on the volume fraction of loaded sorbent.

Summary

The method for reactivity analysis of resin-bonded sorbents and reactive barrier composites is presented. For highly-filled resin-bonded sorbents, the sorbent loading and the high matrix permeability are critical for faster sorption performance, while the layer reactivity is of lesser importance. For diluted reactive barrier composites used as permeation barriers, the high barrier reactivity obtained by reducing the mean particle size is most important for their barrier performance. These results provide directions for better design of reactive and adsorbing polymer composites for controlling contained automotive environments.

References

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3. Solovyov, S.E.; Powers, T.H.; Williams, J.A.; Koch, P.E. Reactive Barrier Composites: An Alternative to Passive Packaging Barriers, Proceedings of Annual ICCE Conference, ICCE-14, Boulder CO, July 2-8, 2006.