

Influences on Barrier Performance of UV/EB Cured Polymers

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Abstract:

The use of UV/EB cured materials as barriers against moisture vapor and/or oxygen gas has long been discussed. Depending on the final requirements and thickness of application, UV/EB materials can be successfully used for this application. Unlike some polymer chemistries and films, UV/EB cured polymers cannot be classified together in terms of barrier performance. Backbone chemistry, molecular weight, functionality, concentration of monomers or oligomers, hydrophobic/hydrophilic balance, density, cure conditions, and the presence of additives or fillers all play a vital role in predicting barrier performance. These variables are explored as performance predictors and compared with real barrier testing results.

Introduction:

Moisture vapor transmission is an important criterion for many polymer applications, including food and beverage containers and protective applications for sensitive electronic components such as semiconductors and display components. The requirements for barrier to moisture vapor range from extremely high to moderately permeable. Moisture vapor transmission rate (MVTR) is described as the rate of gaseous H₂O passing through a film or container. MVTR is directly indirectly related to the thickness of the film or container in question. As an example, 1 mil of a standard PET film will have an MVTR of roughly 25 grams of H₂O passing through 1 square meter of PET in one day (25 g_{H₂O}/m²*day). Because the transmission rate is indirectly proportional to the thickness, 5 mils of the same PET will have an MVTR of 5 g_{H₂O}/m²*day. In the English system of measurements, the permeability is defined at 1mil, and therefore the permeability of this PET would be called 25 (g_{H₂O}*mil)/(m²*day). By knowing the permeability of a particular material, the MVTR of that material at any thickness may be calculated using the following equation:

$$\text{MVTR (g}_{\text{H}_2\text{O}}/\text{m}^2\cdot\text{day)} = \text{Permeability (g}_{\text{H}_2\text{O}}\cdot\text{mil}/(\text{m}^2\cdot\text{day)}) / \text{Thickness (mil)}$$

Different methods of describing permeation or MVTR can cause confusion. Relative humidity and temperature of the test being performed, as well as the dimensions of the resulting values, can create large differences in the numbers reported. For example, while PET may typically exhibit 25 (g_{H₂O}*mil)/(m²*day) at 37.8°C and 100% relative humidity, this number drastically decreases at lower humidity levels and temperature. In addition, some industries may report permeability per cm², or by 1mm thickness, or other variations. This PET could have a permeability of 6.35E10⁻⁵ if the value is reported in (g_{H₂O}*mm)/(cm²*day), and even lower at 90%RH and 25°C.

Moisture vapor transmission rate and permeability are important parameters for some polymer applications, and understanding how the values are reported is also important. Results in this paper eliminate the variable of thickness by using permeability (g*mil/m²*day), and are all tested at 100% relative humidity and 37.8°C (100°F).

Experimental:

Twelve different oligomers and several blends were examined for moisture vapor transmission rate and permeability. Each UV curable resin or blend was mixed with 4% photoinitiator (KTO46) and cured about 5 mils thick on polished aluminum, using two passes at 50fpm under two mercury arc lamps (400W/in) in air. The samples were then removed from the aluminum and cut into the appropriate size for moisture vapor transmission testing.

The apparatus used for moisture vapor transmission testing was a Permatran W 3/33 from MOCON. The instrument parameters were: 100% relative humidity, 37.8°C (100°F), and dry nitrogen flow rate of 100 sccm (standard cubic centimeters per minute). Samples were tested in duplicate and the average values taken for the result. The different samples were chosen to illustrate differences in permeability between backbone chemistry, molecular weight, presence of monomer, and crosslink density. A summary of the materials tested is shown below.

Description	Commercial Code	Identifiant
Urethane Diacrylate Oligomer 1	CN964	UA2-1
Urethane Diacrylate Oligomer 2	CN966	UA2-2
Urethane Triacrylate Oligomer	CN971	UA3
Urethane Diacrylate Oligomer	CN991	UA2-3
Hydrophobic Diacrylate Oligomer	CN307	HP1
Hydrophobic Diacrylate Urethane Oligomer	CN310	HP2
Hydrophobic Triacrylate Oligomer	CN301	HP3
Hydrogenated Diacrylate Oligomer 2	CN308	HHP1
Hydrogenated Hydrophobic Diacrylate Oligomer	CN309	HHP2
Hydrogenated Hydrophobic Urethane Diacrylate Oligomer	CN9014	HHP3
Experimental Aromatic Diacrylate Oligomer	NTX7418	Ex-1
Tricyclodecane Dimethanol Diacrylate	SR833S	TCDMDA
Hexane Diol Diacrylate	SR238	HDDA

Samples were allowed to condition on the MOCON apparatus until equilibrium was achieved, typically for 12 to 24 hours. Equilibrium was defined as consistent results over a minimum 3 hour time frame.

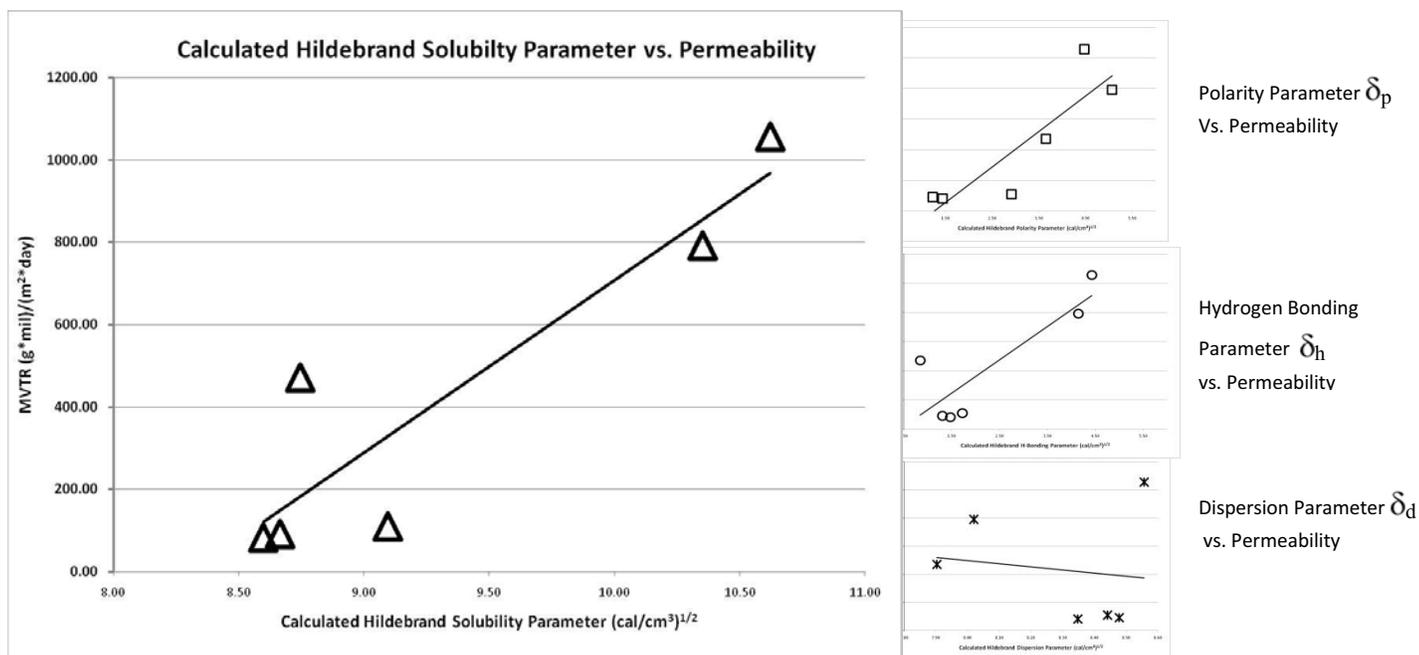
Solubility parameters were calculated using the Hoy group contribution method, and were based on the idealized structure of the synthesized molecules. Unfortunately these are only calculations, and real experimental values would be more accurate for solubility parameters. The author felt that nonetheless, these calculations lent some important insights into the nature of these results, and so they were included despite their inherent imperfections.

Results and Discussion:

Good moisture barrier properties are needed in many applications, and the required performance ranges from low in construction materials to extremely high in OLED barriers. In most cases and for most applications, better performance means better utility.

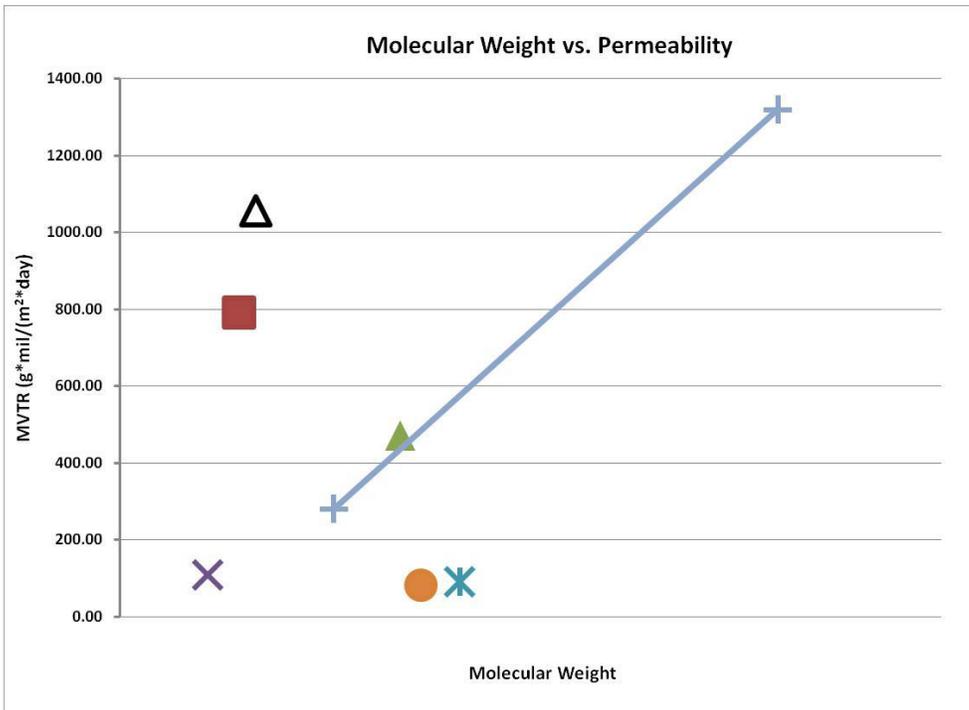
Several structural and chemical parameters had a notable influence on the permeability performance of the UV curable resins tested. Specifically, the four main factors observed contributing to the barrier performance of UV-cured polymers were 1) Hydrophobic/Hydrophilic nature, 2) Molecular weight and crosslink density, 3) Aromatic or cycloaliphatic nature, and 4) presence of unreactive fillers (solid particles).

The first influence readily identified as a major influence on permeability is hydrophobic/hydrophilic nature. HP1, HHP1, HHP2, HP2, HHP3 and HP3 are all on the extremely hydrophobic end of the scale for UV/EB curable oligomers. Materials like UA2-1, UA2-2, and UA3 are also hydrophobic in nature but much less so than the aforementioned structures. Without any regard to the other identified contributors, the graph below depicts hydrophobic nature (calculated Hildebrand Solubility parameters (δ)) vs. permeability for the oligomeric structures tested for this work. It is also interesting to note that some components of the Hildebrand parameter, in particular polarity (δ_p) and hydrogen bonding (δ_h), have more influence over water vapor transmission rates than dispersion (δ_d).



Clearly the implication is that more hydrophobic materials provide a better barrier to the ingress of water vapor. This is as expected, and the correlation to the calculated Hildebrand values serves to identify these calculations as a potential screening tool in the design of new or untested molecules and

commercial products. For the majority of materials tested in these experiments, degree of hydrophobicity was the dominant factor in barrier performance.

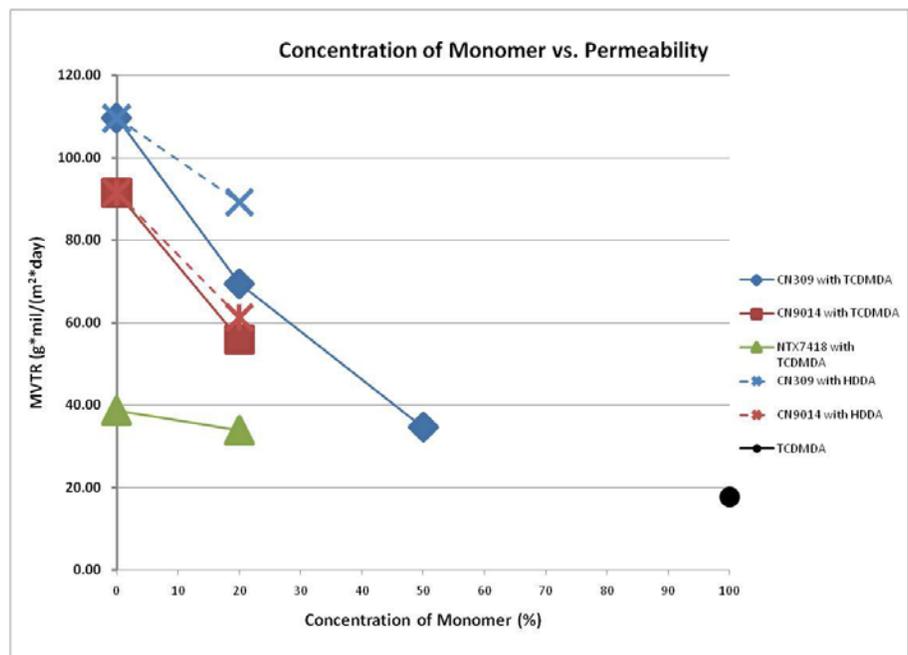


The second major influence on moisture barrier performance is molecular weight and crosslink density. Two oligomeric diacrylates with the same backbone chemistry, but different molecular weights, were tested in the same manner. The lower molecular weight material exhibited much better barrier properties than the higher molecular weight oligomer. Backbone chemistry and the related degree of hydrophobicity had a much larger effect on barrier performance, but within the same backbone chemistry, lower molecular weight or

shorter distance between crosslinks predicted barrier improvement. For dissimilar materials, no real correlation could be made between barrier performance and molecular weight.

An easier way to evaluate effect of crosslink density is to add varying concentrations of a low

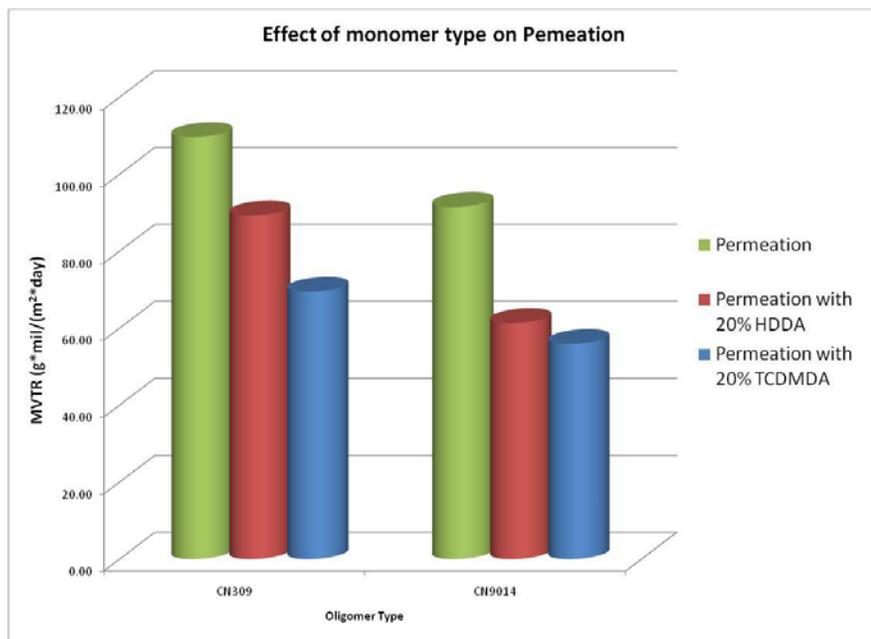
molecular weight diacrylate to increase crosslink density. In this experiment, hexanediol diacrylate (HDDA) was added at 20% by weight to some of the oligomers to observe the effect. In all cases the permeability decreased with the presence of HDDA, indicating that higher crosslink density and a tighter cured network improves barrier performance. In addition to HDDA, another monomer, Tricyclodecane Dimethanol diacrylate (TCDMDA) was added for comparison. The presence of TCDMDA, like HDDA, increased the crosslink density of the cured polymer and boosted the barrier performance. Both TCDMDA and HDDA



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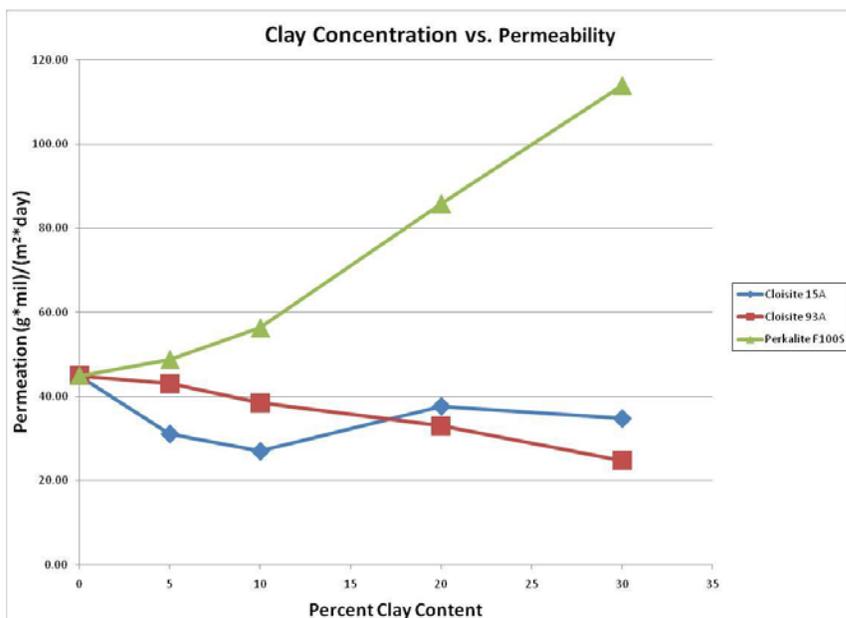
are hydrophobic, but to a much lesser degree than the extremely hydrophobic oligomers and therefore this effect can be contributed more to crosslink density and tighter network formation than to backbone chemistry and hydrophobicity.

The next major contributor identified was the presence of aromatic or cycloaliphatic components in the cured polymer. Apparently both aromatic and cycloaliphatic groups improve barrier properties of similarly structured materials. A good example of this is the influence of HDDA vs. TCDMDA. As has been shown, lower molecular weight materials typically reduce permeability more effectively than higher molecular weight, but in this comparison TCDMDA has a greater efficacy than HDDA, despite higher molecular weight (305 Daltons vs. 226 Daltons). Also interesting to note is that the number of carbons



between acrylate groups for TCDMDA vs. HDDA is similar (7 vs. 6 respectively); therefore, the actual crosslink density is more similar than the molecular weight would suggest. Apparently the cycloaliphatic and more bulky backbone of TCDMDA better discourages ingress of H₂O. At this point it should be noted that TCDMDA alone exhibited the best barrier performance – 17.8 (g*mil)/(m²*day) of any material tested in this experiment. Most likely this is due to the high crosslink density of the low molecular weight difunctional monomer and the overwhelmingly cycloaliphatic nature of its backbone. A second, similar experimental material called Ex-1 also exhibited good barrier performance (38.8 (g*mil)/(m²*day)) and contains aromatic rings in its backbone.

Lastly, the presence of unreactive fillers can influence the barrier properties of UV/EB cured polymers. In this paper several clay materials were tested at different concentrations. At some loading a benefit was seen in the form of reduced permeability but also the type of clay had a large effect on the results. Other more effective fillers certainly can be used but this is outside the scope of this paper. Indeed, an entire paper devoted to the study of various fillers and loadings could easily be justified.



Here, three different clay products were tested at 5%, 10%, 20%, and 30% loadings by weight. It should be noted that there was a dramatic effect on viscosity at 20% and 30% loadings. As viscosity becomes higher, free films are more difficult to cast without any imperfections that can adversely affect barrier performance.

Conclusion

The evaluation of the permeability of UV/EB cured polymers has illuminated several different influences on their performance. In particular, hydrophobicity, high crosslink density, and rich aromatic/cycloaliphatic content seem to factors in providing the best barrier performance. In addition, the use of unreactive fillers can provide a performance boost, although this is not universal, and the types and concentration of fillers have not been exhaustively researched.

The other aspects of the polymer that are needed should also be addressed. The best performing polymer in this study, TCDMDA, does not have all of the ideal polymeric behaviors that are needed for every application. TCDMDA is very brittle and hard, with a high tensile strength and Tg. While this could be ideal for some applications, for flexible packaging for example, the properties are not ideal. Due to the high crosslink density of TCDMDA, shrinkage amounts can be high and coatings thicker than 3-5 mils may crack simply from the polymerization/curing reaction.

Further work is planned to better explore other formulations and blends of materials containing TCDMDA. In addition, the effect of curing parameters will be explored.