Structure-property models for transport in evolving polymer matrices

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Abstract

The transport of small molecules through polymer matrices is a key characteristic of many material systems, from drug delivery devices to latex paint film formation. While first-principles based transport and diffusion models exist, these do not readily allow for treatment of a polymer matrix that is dynamically changing. Descriptor-based models for transport through evolving polymer matrices that will enable subsequent material system design, such coatings with controlled volatility profiles during cure, or drug delivery systems with an optimized drug release rate. This work combines thermogravimetric analysis of volatile compounds and latex-based paint formulation components to study time and temperature dependent curing and evolution of volatiles.

Introduction

What is a VOC?

Volatile organic compounds (VOCs) are compounds emitted or released from solid or liquid mixtures due to their low vapor pressure. Upon release, these compounds participate in photochemical reactions, increasing the amount of ozone in the Earth's atmosphere, which can result in increased levels of smog pollution as well as respiratory health issues.

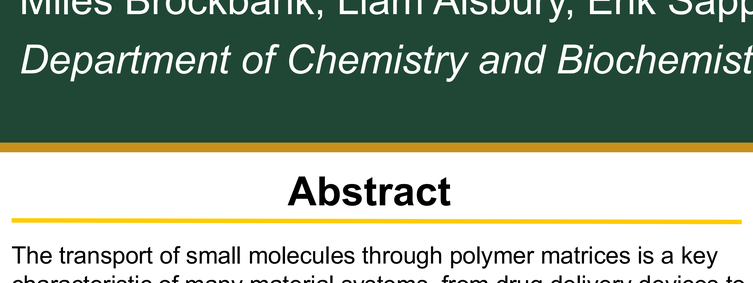


Figure 1. VOC Determination Test Methods. From left to right: TGA control arm loads sample onto hanging balance, ASTM D2369 samples in aluminum pans, and a gas chromatograph mass spectrometer (GC-MS), used in ASTM D6886.

Test Methods: Determining VOC Content

Current methods to assess VOCs in the United States include ASTM D2369, where samples are heated in a pan at 110˚ C for 60 minutes, and D6886-18, a direct gas chromatography method. While the GC method determines VOC content more accurately, the coatings industry prefers the traditional oven method for its simplicity, despite its large margin of error in determining weight percent volatile content. Thermogravimetric analysis, or TGA, is another strategy in determining volatility, aimed at measuring mass against temperature of a sample's surroundings and consists of a highly sensitive balance within a furnace. This method is at the core of our volatility research, providing large amounts of data not obtainable through alternate methods like ASTM D2369.

Current Development

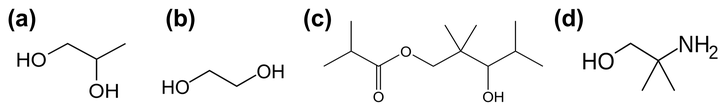


Figure 2. Molecular structures displayed for volatile compounds (a) Propylene glycol, (b) Ethylene glycol, (c) Texanol, (d) AMP95.

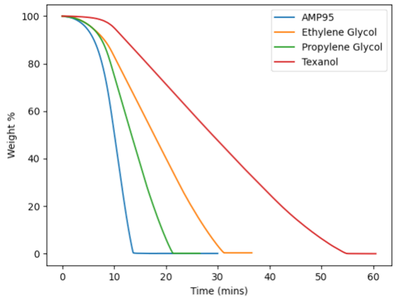


Figure 3. Pure Volatile Compounds TGA Study. Weight percent of four volatiles shown over the course of one hour at 110 ºC.

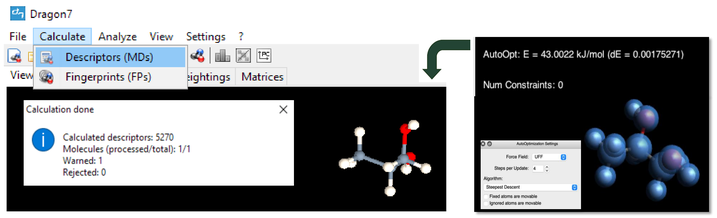
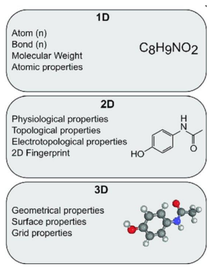


Figure 4. Optimizing Molecular Geometry and Generating Descriptors. Using Avogadro software, volatile structures were optimized with a Universal Force Field (UFF). Dragon7 software was used to calculate descriptors from optimized molecular geometries and other properties. The process for propylene glycol is shown above.



=CORREL(E2:E19,$GUA$2:$GUA$19)

	MW	time_to_zero
Texanol	216.36	55
PG	76.11	22
EG	62.08	31.304
AMP95	89.16	16
MEK	72.12	3.1
IPA	60.11	7.1
Ethanol	46.08	4.22
Diethyl Adipa	202.28	75.83
Acetone	58.09	2.296
Surfynol 104	226.4	66.904
MIBK	100.18	6.521
Methanol	32.05	10.571
Heptane	100.23	4.4541
Hexane	86.2	2.6958
THF	72.12	3.854
Toluene	92.15	5.4375
Vinyl Acetate	86.1	3.52
MeP	270.51	7.079

TDB09v	0.97531277
TDB08v	0.96416343
H7s	0.96115306
RDF095u	0.95647843
RDF085m	0.95427857
DP10	0.95148212
SpMax7_Bh(	0.95120263
DP11	0.94994203
H8s	0.94955591
DP09	0.94915109
TDB08e	0.94885765
TDB10s	0.94856559
DP12	0.94684711
IC2	0.94657531
SM5_D	0.9461295
GMTIV	0.9450958

Figure 5. Descriptor Correlation Analysis. Excel was utilized to correlate descriptor values with variables of volatility. The most promising Pearson correlation coefficients (shown on the right) emerged when relating descriptors to the time it took to reach 0% mass.

```
X = df[["H7s","IC2","ATSC5p","DELS","ATSC3p","ATSC2p"]]
Y = df[["time_to_zero"]]
```

```
X_train, X_test, Y_train, Y_test = train_test_split(X, Y)
```

```
ttt_model = LinearRegression()
ttt_model.fit(X_train, Y_train)
```

DELS	DELS
19.666	0.960958
8.009	0.391351
6.500	0.317615
7.125	0.348155
5.625	0.274860
4.111	0.200880
3.139	0.153384
20.465	1.000000
4.889	0.238896
17.509	0.855558
6.681	0.326460

Train-Test-Split

Descriptor values were first normalized (shown for DELS: molecular electrotopological variation) and then the data was separated into two sets: One trains the model, while the other is used to test the trained model's predictions. From this, predicted data was compared to measured data (actual time to zero % weight) to indicate our model's efficacy.

Current Development

Train-Test-Split into Structure Property Modeling

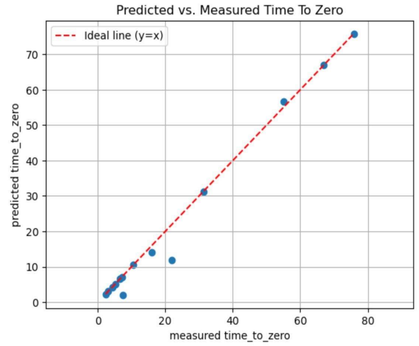
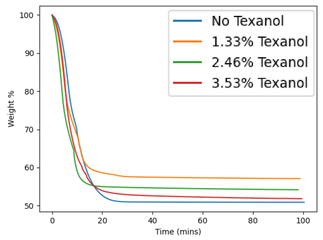


Figure 6. Predicted against measured volatility. The time for each sample to reach 0% mass was predicted using descriptor values available in the test-split, then graphed against the real-world values for time to 0% mass for respective samples run by TGA. Upon incorporation of additional data, the training/test sets were shuffled, and the results changed each time. This predicted versus measured volatility graph yielded a trendline with an R^2 value of 0.922.

Future Directions



RUN3

	pan(w/ pclip)	pan+sample	pan+solids	fraction solids
SG30	1.6896	2.22042	1.95093	0.4923
SG30 1.33% tex	1.68502	2.207	1.943	0.4942
SG30 2.46% tex	1.69094	2.30836	1.99005	0.4845
SG30 3.53% tex	1.6884	2.21539	1.94329	0.4837

RUN4

	pan(w/ pclip)	pan+sample	pan+solids	fraction solids
SG30	1.69131	2.24773	1.96479	0.4915
SG30 1.33% tex	1.68117	2.25854	1.963	0.4881
SG30 2.46% tex	1.66993	2.24386	1.949	0.4862
SG30 3.53% tex	1.68174	2.25735	1.96115	0.4854

Figure 6. TGA testing compared with ASTM D2369 testing. (L) Rhoplex SG30 resin samples with varying amounts of Texanol tested in TGA for 100 minutes at 110°C, with **(R)** an oven for 60 minutes at 110°C (ASTM D2369)

Upcoming Mixture Research

Further TGA testing of similar resin mixtures will combine correlation analysis of component volatility with QSAR modeling to determine relationships between complex mixture contents and volatility behavior, like latex formation during heating and its effects on additives' ability to escape. In short, new QSAR/QSPR models will investigate VOC transport in evolving polymer matrices.

Acknowledgments

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References

1. *Todeschini, R., & Consonni, V. (2009). Molecular Descriptors for Chemoinformatics: Volume I: Alphabetical Listing (2nd ed., Vol. 41). John Wiley & Sons, Incorporated.*