Measuring Volatiles from Radiation-Curable Acrylate Monomers, Oligomers and Blends

*Robin E. Wright/*3M *Corporate Process Technology Laboratory/St. Paul, MN*

Introduction

Radiation-curable coatings comprising acrylate monomers, oligomers and blends are becoming more prevalent in industrial applications because they can be coated solvent-free reducing environmental impact, cure fast increasing productivity, and give superior properties providing competitive advantage. In addition, most raw materials are available globally which allows local sourcing.

The purity of the raw materials used in a coating formulation can have a noticeable impact on product performance, however. Impurities may include trace amounts of residual solvent, non-polymerizable monomer precursor species and impurities carried over from inadequately cleaned kettles used for synthesis. Their presence can cause increased odor, an increase in downtime and product rejects in production as well as an increase in customer complaints.

A typical MSDS for an acrylic monomer or oligomer contains information related to physical properties such as specific gravity, viscosity and vapor pressure. Monomer purity is often reported as a minimum percentage or an approximate percentage. No supplier of acrylate monomers or oligomers currently provides any emissions data because, until now, there has been no established test method available.

As a result, while radiation-cured coatings are clearly low VOC when compared to alternatives, early adopters of UV technology and suppliers of UV-curable resins and formulated coatings used phrases like “zero-VOC,” “100% solids,” “negligible” and “no VOCs” to emphasize the environmental advantages of UV curing. The tendency of quartz windows to foul over time in production environments, however, clearly suggests that these claims were not entirely true.

ASTM test method D7767-11 allows for a quantitative measure of the volatile content of radiation-curable acrylate monomers and oligomers as well as acrylate blends.[1] The data obtained can be used to assist suppliers in checking lot-to-lot variability and effects of process changes, assist formulators in selecting raw materials, assist end users to better control production processes and reduce emissions, and assist consumers by improving product performance and consistency.

A list of monomers tested during the development of this test method is shown in Table 1. The results indicated that the percent total volatile content showed an inverse relationship with acrylate functionality - higher functional monomers had lower volatile content. This is consistent with what one would intuitively expect based on the monomer molecular weight and

the probability that a given monomer molecule would be tied into a crosslinked network structure during the polymerization process.

Table 1
Percent Total Volatile Content of Some Common Monomers[2]

Resin	Functionality	Total Volatile (%)	St. Dev. (%)
octyl/decyl acrylate	1	4.54	0.08
decyl acrylate	1	4.39	0.10
2-ethylhexyl acrylate	1	4.23	0.04
benzyl acrylate	1	2.40	0.08
2-phenoxyethyl acrylate	1	2.13	0.07
tetrahydrofurfuryl acrylate	1	2.00	0.02
cyclohexyl acrylate	1	1.58	0.06
tripropyleneglycol diacrylate	2	1.20	0.27
neopentylglycol diacrylate	2	1.15	0.16
acryloyl morpholine	1	0.52	0.08
trimethylolpropane triacrylate	3	0.40	0.04
pentaerythritol triacrylate	3	0.10	0.02

In this study, the volatile content of monomers from different suppliers and multiple lots of the same monomer from a single supplier are presented. The results show that the data from ASTM D7767-11 are more than just numbers on an MSDS and that the information can be used to improve product performance and consistency.

Experimental

Samples of common monomers were obtained from three different monomer manufacturers. When available, multiple lots of the same monomer from a single manufacturer were obtained. All monomers were used as received without further purification.

19.6 grams of each sample to be tested were added to amber vials containing 0.4 grams of TPO-L (available from BASF) and the mixtures rolled overnight. Each sample was then tested in triplicate per ASTM D7767-11 Method A. Table 2 lists the monomers along with the abbreviations for each used throughout this paper.

Irradiation was performed using a Hamamatsu Model L9566-01 Lightningcure™ 8 UV source with a 200W Xe/Hg lamp equipped with a 5mm diameter quartz fiber guide.[3] Sample irradiance and energy was measured using an EIT PowerPuck II radiometer.[4] A standard exposure condition of 80.0 seconds at a UVA peak irradiance of 100-110 mW/cm^2 was used.

Table 2
List of Monomers Tested

Chemical Name	Abbreviation
ethoxyethoxyethyl acrylate	EOEOEA
hexanediol diacrylate	HDDA
isobornyl acrylate	IBOA
isooctyl acrylate	IOA
neopentylglycol acrylate	NPGDA
octyl/decyl acrylate	ODA
2-phenoxyethyl acrylate	PEA
tetrahydrofurfuryl acrylate	THFA
tripropyleneglycol triacrylate	TPGDA

Results

The percent total volatile content of the monomers tested according to ASTM D7767-11 Method A are shown graphically in Figure 1. Note that the new test method does not measure the percent of volatile organic content or VOC's as any measured weight loss will include water and other non-VOC solvents such as acetone that may be present.

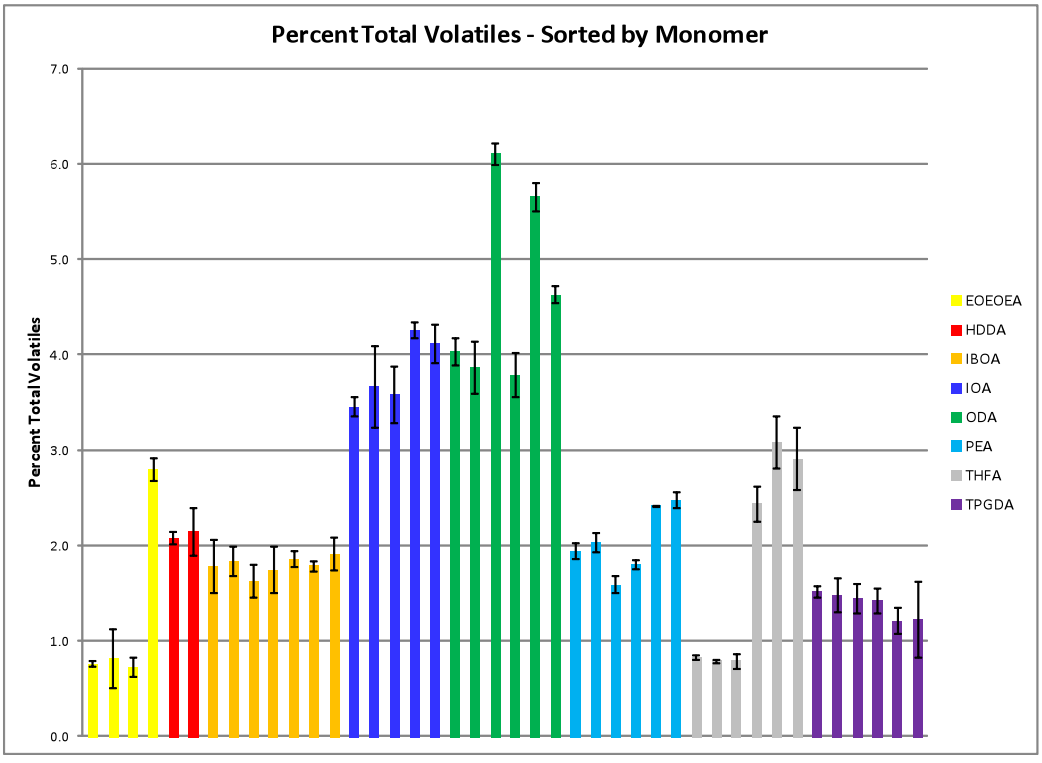

Figure 1. Percent total volatile content of monomers grouped by monomer.

The data show that the volatile content of monomers from different manufacturers determined using ASTM D7767-11 can be similar or can vary dramatically. The data also include results from testing a couple of monomer lots that were either expired or near their expiration date.

Figure 2 shows the same data by monomer but grouped by manufacturer which shows more clearly the differences between manufacturers and lot-to-lot differences for the same manufacturer. Note that like colors within a chart indicate the same manufacturer but like colors between charts have no relationship as to a specific manufacturer.

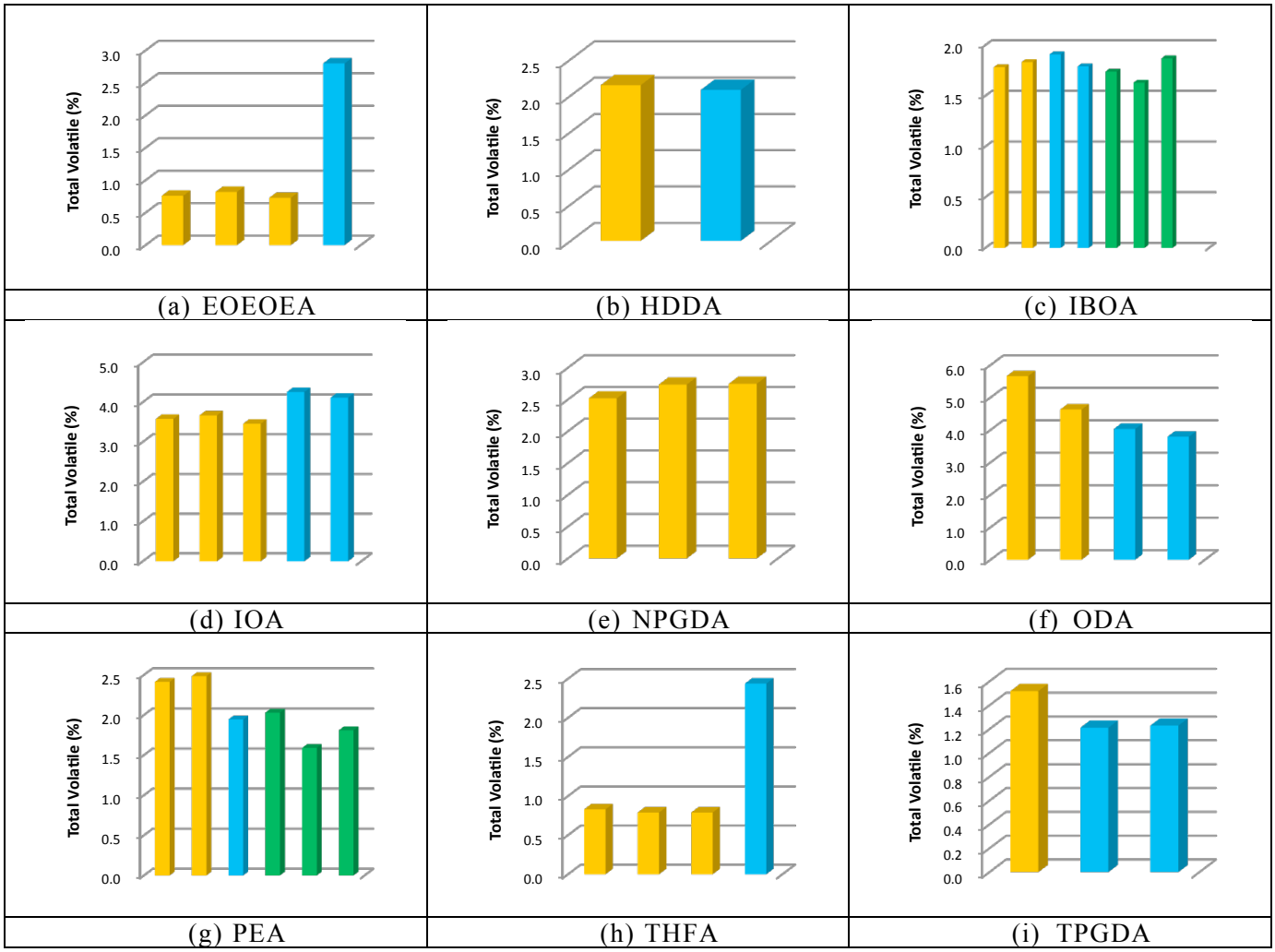

Figure 2. Percent total volatile content of monomers by manufacturer.

All of the data shown in Figure 2 were measured on fresh samples provided by the manufacturers and presumably less than one year old. Some older monomer samples available in our lab were also tested but the results are not shown in Figure 2. The effect of aging was a higher percent total volatile content value indicative of lower conversion, more unreactive species present or possibly some contamination issues. No attempt was made to determine the actual cause.

It is difficult to ascertain whether any apparent differences between manufacturers are statistically significant or not due to the limited sampling done. However, statistical analysis of the means for the THFA data from the two manufacturers shown in Fig. 2(h) confirm that the samples are statistically different.

Conclusions

The new test method ASTM D7767-11 Method A has been used to compare the percent total volatile content from several common monomers obtained from different global suppliers. Because of differences in starting material purity, synthetic scheme, process conditions, solvents used, purification procedures and sources of contamination, it has been shown that under a specified set of cure conditions, the percent total volatile content of the monomers can vary dramatically. In addition, for the few aged samples tested, sample aging appears to also have an effect on the percent total volatile content.

The percent total volatile content results provided by this simple testing procedure can serve as an additional piece of information used by monomer manufacturers as both a consistency check on their products and as a measure of the impact that any process changes may have. The data can also be used by formulators to select raw materials and verify their source of supply. End-users will benefit by knowing that they will be less likely to experience unforeseen problems due to upstream changes in their supply chain. Finally, end users will benefit by being able to obtain products having UV/EB coatings with better performance, lower odor, and more consistent properties.

ASTM D7767-11 also provides a method to utilize the information obtained from Method A to calculate a percent total volatile content for a coating based on composition. Thus, if a coating was comprised of a 50:50 blend of Monomers X and Y which had an individual percent total volatile content of 2.6% and 1.2%, respectively, then the 50:50 blend would have a calculated percent total volatile content of 1.9%.

A more preferred method would be to take the 50:50 blend of Monomer X and Y and run the Method A test on the blend itself. This will typically result in a lower percent total volatile content value because of the synergistic effects that can occur when blends are cured.

Acknowledgements

The author would like to recognize and thank BASF, Cytec Surface Specialties, Cognis, Nazdar, San Esters, and Sartomer for their participation in the round robin required as part of the ASTM approval process and/or for providing samples for the study reported here.

References

[1] ASTM D7767-11 “Standard Test Method to Measure Volatiles from Radiation Curable Acrylate Monomers, Oligomers, and Blends and Thin Coatings Made from Them” is the property of ASTM International. Copies can be obtained at www.astm.org.

[2] RE Wright, MB Baker, RK Swanson and RL Walter, “Estimating Emissions from Thin Radiation-Curable Coatings,” RadTech Report September/October 2008.

[3] available from Hamamatsu USA, Bridgewater NJ.

[4] available from Electronic Instrumentation Technology, Sterling, VA.