WHITE PAPER – Rob Lorenzini, PH.D. - Barentz

VOC Reducing Additives for Masterbatches and Final Polymer Articles

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Abstract

The reduction of VOCs (volatile organic compounds) in polymers is becoming more important as many automotive producers and OEMs are seeking to meet stringent specifications regarding VOCs in automobile cabins. In addition, "cosmetic organoleptics", or the aesthetic lack of plastic smell, are becoming more important as polymers continue to replace other materials such as metals, and as consumers remain generally wary of polymers in their lives from a health and safety perspective. Herein, synthetic aluminosilicate polymer additives are shown, quantitatively, to reduce the VOCs/odors resultant from processing and the end-use of polymeric articles. Various gas chromatography experiments are utilized to quantitatively show the chemical species that are captured by this powerful additive, as well as human sniffing testing to qualitatively show the effects on the perceived odor. In addition to size exclusion mechanisms, this synthetic mineral additive derives its specificity from the inherent hydrophilic/hydrophobic nature of the different zeolite crystal lattices.

Introduction

Synthetic zeolites are porous aluminosilicate minerals that have long been utilized within various industrial processes, such as: gas separations, water softening, catalysis, ion-exchange, and others.[1] Their inert nature, as well as their high porosity, surface area, and adsorption capacity, make them ideal materials to adsorb various small molecules, even when incorporated within a polymer matrix. More than 60 naturally-occurring zeolites, such as clinoptilolite and chabazite, have been discovered worldwide,[2] and many synthetic versions have been produced in commercial quantities since the 1950s.[3] Synthetic zeolites have advantages over natural zeolites, including: larger pore sizes not found in nature, higher consistency, higher purity, and the ability to reliably tune affinity for various molecules to be adsorbed.[4]

Common molecular sieves are known to lever their affinity to capture small molecules by changes in the pore size, influenced by cation selection, silicon/aluminum ratios, and the addition of other metal oxides, operating chiefly on a size-exclusion mechanism [Figure 1]. Pore size is determined by the number of oxygen atoms surrounding the pore, as well as the pore's inherent shape. More specifically, the aluminum and silicon tetrahedral atoms form a 3D framework of AlO_4 and SiO_4 tetrahedra linked together by shared oxygen atoms, and the pore volume and geometry is determined by the specific topology in the crystal lattice.[5] Specialty zeolites can achieve more specificity than size-exclusion alone by levering the polarity of the material. This is achieved by adjusting ratios of different zeolites to change the inherent hydrophobicity or hydrophilicity of the blend [Figure 2].

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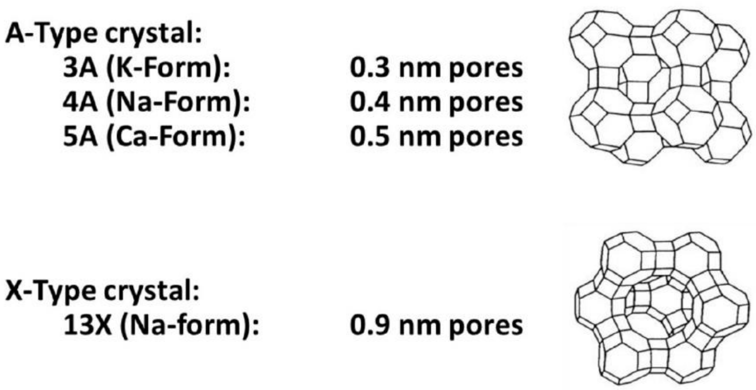

Figure 1 – Zeolite pore size varies depending on the crystal polymorph

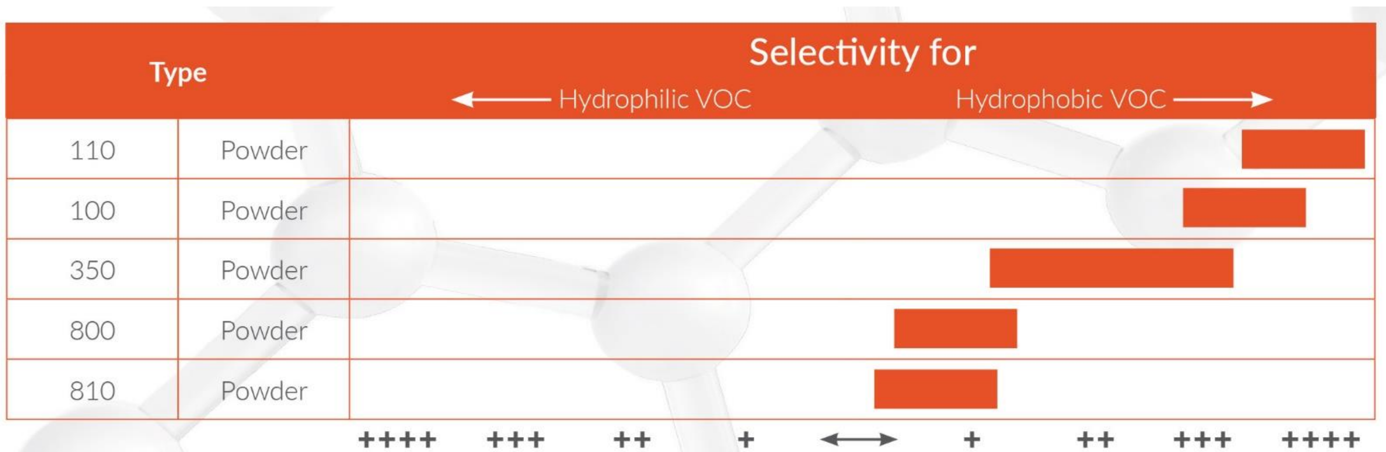

Figure 2 – The polarity of zeolites can be adjusted to enhance selectivity for VOC adsorption

The high adsorption capacity of synthetic zeolites make them useful for the removal of volatile organic chemicals (VOCs) from polymers. The demand for additives with this function has increased in recent years, primarily from the implementation of stringent VOC requirements from automobile producers for polymers and coatings used in the passenger cabin. Additionally, as consumers remain generally wary of polymers from a safety perspective (e.g. bisphenol A in polycarbonate water bottles), the reduction of "plastic odor" resultant from polymer or additives will help ease concerns in applications where polymers are replacing other materials, or in high-end polymer articles where odor is unacceptable. Zeolites are effective at adsorbing a wide variety of aliphatic and aromatic organic compounds, including especially pungent sulfur-containing molecules such as thiophenes,[6] dimethyl sulfide, and mercaptans.[7] This adsorption robustness has been demonstrated in the literature with success in polymer applications ranging from removing odors in food packaging,[8] increasing the time to rotting in PE strawberry packaging by managing ethylene,[9] scrubbing furfural, limonene, and other VOCs from two natural flour-filled PPs,[10] and even in the selective elimination of creatinine from kidney failure patients in zeolite/EVOH fibers.[11] Other adsorbent materials, such as alumina and activated charcoal, have been shown to have both lower adsorption enthalpy (less favorable adsorption) and capacity than synthetic zeolites.[12]

VOC Reduction in Various Polymer Systems

Acrylonitrile Butadiene Styrene (ABS)

1% of two synthetic zeolite products were compounded into ABS, and were subject to VDA277 VOC testing, a common gas chromatrographic (GC)/flame ionization (FID) detector headspace method used in the automotive industry. Testing to this specification first entails making various calibration solutions of acetone in butanol. Next, a known amount of pulverized polymer is put in a headspace vial, and the samples are conditioned at 120°C for five hours. After conditioning, 1mL of headspace gas is injected into the GC, where analytes are separated by a wax column of specified dimensions. The GC oven is ramped, and materials are separated and then pass through a flame ionization detector. Materials qualify as VOCs depending on the number of carbon atoms in their backbone according to the standard. Tests were run in triplicate and the results were averaged. The overall carbon emission data is summarized in the table below [Table 1].

Sample	Total Carbon Emission (ugC/g)	Standard Deviation (ugC/g)	% VOC Reduction
ABS	59.0	1.6	--
ABS + 1% ZEOFlair® 100	54.0	2.0	8.5
ABS + 1% ZEOFlair® 810	43.9	0.8	25.6

Table 1 – Reduction of carbon emission in ABS in accordance with VDA277

The reduction of selected VOCs are shown below [Table 2]. For ABS, the more effective zeolite was intermediate on the hydrophobicity scale – the more hydrophilic ZEOflair® 810 adsorbs ~3x more carbon emission than the hydrophobic ZEOflair® 100. The largest reduction by percentage was acrylonitrile, which went from ~5 µgC/g to an undetectable level. This result can be rationalized by the fact that acrylonitrile is a fairly hydrophobic compound, with ~70g/L solubility in water.

	Emission, µgC/g		
Compound	ABS	ABS + ZEOFlair® 100	ABS + ZEOFlair® 810
isobutene	0.7	0.6	0.4
1,3-butadiene	0.2	0.1	0.0
acetaldehyde	0.3	0.2	0.0
acrolein	0.2	0.1	0.0
ethanol	1.0	0.7	0.0
acrylonitrile	4.7	3.9	0.0
styrene	10.3	9.3	6.9
α-methylstyrene	30.4	28.7	25.0

Table 2 – Specific VOCs removed from ABS by synthetic zeolites

Polypropylene (PP)

Polypropylene degradation involves the oxidation and cleavage of the polymer chain. Small molecules formed during thermooxidative degradation include acids (oxalic, formic, acetic), ethers, esters, aldehydes, alcohols, alkanes, alkenes, and others. Again, 1% of two synthetic zeolite products are extruded into PP and are subject to VDA277 testing [Table 3].

Sample	Total Carbon Emission (µgC/g)	% VOC Reduction
PP	16.0	--
PP + 1% ZEOFlair® 100	10.9	31.9
PP + 1% ZEOFlair® 810	10.8	32.5

Table 3 - Reduction of carbon emission in PP in accordance with VDA277

In this case, there is parity between the more hydrophobic and hydrophilic zeolite formulations. The reduction of selected VOCs are shown below [Table 4]. The complete

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elimination of a few alkanes and alkenes is noted. Interestingly, the relatively hydrophobic alkanes and alkenes showed greater affinity for the hydrophilic zeolite than the hydrophobic grade. This could be rationalized with the assumption that the greater affinity for water vapor helps as a "carrier" to penetrate the zeolite pores more deeply.

	Emission, µgC/g		
Compound	**PP**	**PP + ZEOFlair 100**	**PP + ZEOFlair 810**
isobutene	0.5	0.4	0.3
2,2-dimethylbutane	0.2	0.0	0.0
3-methylpentane	0.6	0.0	0.0
1-hexene	0.2	0.0	0.0
3-methyl 1,4-pentadiene	0.2	0.1	0.0
acetone	1.2	0.3	0.0
n-butyralaldehyde	0.1	0.0	0.0

Table 4 - Specific VOCs removed from PP by synthetic zeolites

In another series of experiments, polypropylene is filled with hemp, which is an eco-friendly cellulose-based fibrous filler used in the automotive industry. Synthetic zeolites are extruded in at various concentrations, and the compound is subject to dilution dynamic olfactometry. In this test, the compounded material is conditioned with heat, and successive air dilutions are performed on the headspace of the samples. The units of this test, European odor units/m3 (OUE/m3), is defined as the amount of "plain air" required to dilute the odorant to a barely perceptible level.[13] A trained examiner's olfaction is used for the evaluation, with specific criteria on how to choose an appropriate panel of sniffers. The more hydrophilic zeolite was chosen for this evaluation due to the polar nature of the hemp fibers, and the olfactometry data is shown below [Table 5], where the zeolite-containing sample is shown to reduce the odor by over 50%.

Sample	Odor Concentration (OUE/m3)	% Reduction
PP	100	--
PP + Semi-Retted Hemp	2140	--
PP + Hemp + 1.0% ZEOFlair® 810	1000	53.3

Table 5 – Olfactometry data for semi-retted hemp-filled PP

Polyvinyl chloride (PVC)

PVC is known to be an odorous polymer due to residual pungent monomer, small molecule degradation products, plasticizer, heat stabilizers, and other additives.[14] An internet search yields many results for consumer worry about the safety these odors, whether justified or not. Here, the ability to scrub VOCs before they reach the consumer's nose (or "cosmetic organoleptics") would help acceptance of the use of this low cost, highly versatile polymer. The results from dynamic olfactometry according to EN13725 after 24 hours of sitting in an impermeable bag, as well as GC/FID according to VDA277, are shown in the table below, demonstrating a reduction in odor by ~60% and VOCs by ~20%, respectively. [Table 6].

Sample	Total Carbon Emission (µgC/g)	% VOC Reduction	Odor Concentration (OUE/m³)	% Odor Reduction
PVC	15.5	--	170.0	--
PVC + 1% ZEOFlair® 110	11.9	23.2	70.0	58.8

Table 6 – Reduction in total carbon emission according to VDA277 and odor according to EN13725 using synthetic zeolites

Polylactic Acid (PLA)

Biopolymers are becoming more relevant as the call for renewable resources increases from both consumers and legislation. Although imperfect in terms of long-term stability, they are finding various applications across industries. Again, the more hydrophilic zeolite was selected for testing due to the polarity of the polymer and therefore the expected polarity of the degradation products. The results from a dynamic olfactometry measurement in 10% cellulose-filled PLA accordance with EN13725 is shown in below [Table 7], showing a ~70% reduction in odor.

Sample	Odor Concentration (OUE/m³)	% Reduction
PLA + 10% Cellulose	1600	--
PLA + Cellulose + ZEOFlair® 810	500	68.8

Table 7 – Reduction in odor in cellulose-filled PLA with synthetic zeolites

Polyphenylene Sulfide (PPS)

PPS contains a thioether within the polymer backbone, which can be cleaved during thermoxidative degradation to form sulfur-containing molecules small enough to reach the nose. Data were generated from a GC/MS sniffing analysis in accordance with ISO16000-6 after conditioning for 2 hours at 80°C. In this test, VOCs are introduced to a sorbent, then the material is desorbed with heat and run through a GC/MS or GC/FID to separate and identify the VOCs. Results from this test method report the overall intensity as well as the individual odor "notes" according to the standard. In this case, the overall intensity of odor was reduced from 3.0 to 2.5, as well as the elimination of gasoline notes and reduction of sulfur and phenolic notes. VOCs that were completely eliminated include various aliphatic and aromatic species, as well as thiophene derivatives.

Conclusions

Synthetic zeolites were demonstrated to reduce and/or eliminate different VOCs from various polymer systems, namely: ABS, PP, PVC, PLA, and PPS. Industrially-accepted, standardized test methods were utilized to quantitatively demonstrate the function of these additives. The affinity for different VOCs is levered in the ZEOFlair® products by pore size, as well as hydrophobicity/hydrophilicity by changing the starting materials that make up these synthetic aluminosilicates. Overall reduction in VOCs were shown to range from the single digits to over 50% depending on the VOC, polymer system, and analytical method. Further quantitative work is being undertaken in different polymer systems, and will be disseminated to the technical community in a later conference publication. The potential to reduce VOCs and odors with these additives are as limitless as the imagination – compatibility and effectiveness has been demonstrated in polymers that are wildly different in terms of atomic composition, polarity, inherent stability, and applications.

Acknowledgements

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