WHY QUALITY OF TACKIFIER RESINS MATTERS IN DEVELOPING SPECIALTY TAPES

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Introduction

The performance requirements for tapes and labels are increasing year over year. While customer requirements are pushing the demands being imposed on adhesives tapes, digitization pushes the need for more advanced applications.

For applications in the automotive industry, as well as in the hygiene industry, there is an increasing need for low-odor raw materials. Moreover, low emissions and odor levels are preconditions for tape use in interior applications. In order to understand how to evaluate odor, raw material suppliers must develop new products that are heat stable and do not release odor during storage or usage of the product. For odor evaluation, suppliers must develop olfactory measurements and new analytical techniques that can be used as a proxy for odor of the final product. For odor stability, the products must show low odor not only during the manufacturing process but also during storage under different conditions.

Furthermore, customer awareness and regulatory requirements will further restrict the level of trace chemicals in adhesives systems. Trace chemicals may be present as residual monomers or additives that are used during the manufacturing process. Raw material suppliers need to understand the applicable regulatory requirements and demonstrate that their products will meet these requirements. In addition, there is a trend with more strict requirements being imposed on volatile organic compounds (VOC) and fog levels in raw materials used in the automotive industry. For example, in interior applications, low or even ultra-low VOC levels are extremely important. This is especially true in China, where their government is driving an odor-free agenda [1].

Raw material suppliers must implement methods to measure the VOC and fog levels of products they are producing, and new manufacturing methods must be developed to limit the levels of VOC and fog in their products. Especially for UV curing systems, there is a need for highly purified and stable tackifiers that do not interfere with the UV curing process. The need for high-purity tackifiers poses a challenge on the manufacturing process and analytical methods, especially since some of these raw materials have a natural origin and differ in quality depending on the region of origin.

Demands on adhesive tape performance and the quality of raw materials being used in formulations is increasing. Developing low-odor or low-VOC/fog hot melts and reactive hot-melt pressure-sensitive adhesives (HMPSA) is impossible without the proper set of raw materials. For this reason, raw material suppliers are forced to innovate their portfolio to meet the more stringent demands on low odor, low VOC, low fog, low trace chemicals, and high purity.

New developments and product innovations require a new approach with respect to product evaluations. The latest analytical test methods, coating technologies, and adhesive test methods (including odor, VOC, and fog level testing) are applied to develop the best products for the adhesives industry. Examples of recently developed products with improved performance on odor and VOC levels will be described in this paper.

Background

The relationship between odor and the volatility of chemical compounds is complex [2,3]. Odor is the property of certain chemical compounds in their volatilized form — usually at very low concentrations — that triggers chemical receptors in the olfactory nerve system, enabling humans and animals to perceive a sense of smell. This could be a pleasant or unpleasant smell. Organic molecules that have a high vapor pressure at ambient temperature are called volatile organic compounds (VOCs), and these compounds may or may not be odoriferous themselves. While odor determination is obviously dependent on the observer's sensory perception, VOCs are determined by analytical measurements using specialized equipment.

Malodors or unpleasant smells have a negative reputation in the public opinion and are often linked to chemical constituents within a certain product or confinement. There is growing concern with regard to the potential adverse health effects of chemicals that are released from consumer goods — such as personal care products — as well as from chemicals accumulating in confined spaces, like the interior of a car. While customer requirements are pushing the demands being imposed on products such as specialty adhesives tapes, diapers, and sanitary towels, these public concerns impose significant pressure on marketers, formulators, and raw materials suppliers to come up with solutions to reduce odor and VOC content. The first concerns with consumer goods like diapers and sanitary towels arose in South Korea in 2017, and similar concerns have recently spread to Europe [4]. In response, there is an increasing need for low-odor raw materials for applications in the automotive and hygiene industries.

In addition to understanding how to evaluate odor, raw material suppliers must develop new products that are heat stable and do not release odor during storage or usage of the product. For odor evaluation, suppliers must develop olfactory measurements and new analytical techniques that can be used as a proxy for odor of the final product. For odor stability, products must show low odor during the manufacturing process and during different storage conditions.

Customer awareness and regulatory requirements will further restrict the level of trace chemicals in adhesives systems. Trace chemicals may be present as residual monomers or as additives used during the manufacturing process. Raw material suppliers need to understand the applicable regulatory requirements and demonstrate that their products will meet these requirements. In addition, there is a trend towards more strict requirements being imposed on VOC levels and fog levels, or the sum of the heavy volatile substances, in raw materials used in the automotive industry. Raw material suppliers must implement methods to measure VOC and fog levels of the products they are producing, and new manufacturing methods must be developed to limit the levels of VOC and fog in their products.

The pressure-sensitive adhesives market, with a total adhesives market volume of 133 kMT in 2017, is split among three main categories: automotive, electronics, and medical [1]. With a share of 47 kMT, the global annual growth of adhesives in the automotive market segment is projected at 2.8% for 2017–2022 [1]. In fact, the global automotive adhesive tapes market is expected to reach $11–$12 billion by 2024, according to a report by Grand View Research, Inc. [4]. For the medical market segment, the market volume will be in the order of 46 kMT with a projected global annual growth rate of 4.6% (2017–2022), while for the electronics market segment, this will be around 41 kMT and a global annual growth rate of 3.5% over the same period [1]. Therefore, demand for raw materials such as polymers, tackifier resins, oils, and other additives will also grow.

In this respect, tackifiers are the most important of these after the base polymer, comprising up to 40% of the final formulation. Nonetheless, developing low-odor or low-VOC/fog hot melts and reactive HMPSAs is impossible without the proper set of raw materials. We deploy state-of the-art methods to measure the odor and level of volatile substances (VOC and fog) in an adhesive or tackifier sample and understand their limitations. Furthermore, we consider every chemical component detected in a sample's mixture of volatile substances possesses a unique perceived odor and intensity. Finally, continued work is carried out to reduce any contribution that tackifiers make to the concentration of VOCs and odor in hot-melt adhesives (HMA) formulated with them.

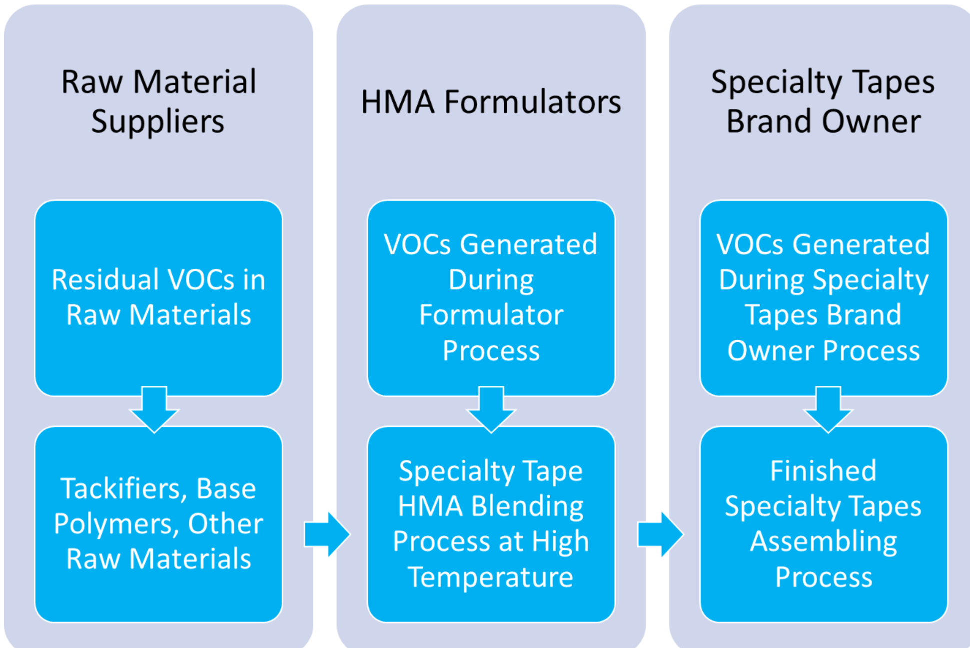

Figure 1. Origin of VOCs from specialty tapes during the entire production process from raw materials to finished goods

The origin of VOCs

The first question to answer is about the origin of such VOCs. Where do they come from? By looking at the overall manufacturing process of a specialty tape as depicted in Figure 1, there are three points of origin for volatile and potentially odor-causing substances:

1. VOCs exist as components of one or more raw materials such as base polymer, tackifier resin, oils, and other additives.

2. VOCs are produced by chemical reactions such as oxidation or decomposition during adhesive formulation, a process that requires heating and shear.

3. VOCs are produced as the specialty tape product is assembled.

To apply the adhesive during tape manufacturing, the coating process onto a suitable backing is normally done at elevated temperatures exceeding 130°C to lower the viscosity sufficiently to improve handling. Volatile substances already present in the raw materials may be released during this coating process, and additional VOCs could be generated by chemical reactions. These substances could either be released by venting to the environment or absorbed by other constituents of the specialty tape, such as the backing or liner, and locked into the final product. If venting is lacking or not sufficient, volatile compounds could also become entrapped when the finished tape is sealed in by its final plastic packaging immediately after production. These volatiles could be released the moment a consumer opens the packaging. Consumers may notice the odor caused by whichever odorous volatile substances are present in concentrations high enough for a consumer to perceive. Based on this information, the ideal HMAs and their constituent raw materials should: (1) contain little or no odorous volatile substances, especially none with proven health concerns, and (2) not be prone to chemical reactions that generate new volatile substances during adhesive blending and application operations.

VOCs and odorous compounds could be released or generated outside of the manufacturing process. For example, during its lifetime, an automotive specialty tape applied near a hot engine surface may generate or release unwanted volatile chemicals and be perceived as odorous and unhealthy.

Odor analysis of raw materials

The need for high-purity tackifiers poses a challenge on analytical methods, especially since some of the raw materials have a natural origin and differ in quality depending on the region of origin. Moreover, odor analysis is complex and depends on many factors. For instance, small amounts of odorous components (as low as sub-ppm level) can have a tremendous effect on the final perceived odor. In addition, odor determination is dependent on the observer’s sensory perception. To reliably evaluate the odor of raw materials, several techniques are required.

During new hydrocarbon resin development, the following techniques have been used:

1. GC-MS headspace analysis
2. GC-MS sniffing (i.e., GC-olfactory (GC-O) detection)
3. Odor panel testing

GC-MS headspace analysis

Headspace sampling is a suitable technique for the analysis of trace amounts of analytes as well as the analysis of volatile species, either quantitatively or qualitatively, that can be efficiently partitioned into the headspace gas volume from a liquid or even a solid matrix. This analysis is of particular interest when only a selected part of a sample should be injected onto the column of a gas chromatograph. One way to obtain detailed information about entrained or generated volatile substances is to heat a material of interest inside a sealed container (e.g., a vial as depicted in Figure 2), collect a sample of the vapor that accumulates in the headspace, and analyze the vapor by tandem gas chromatography followed by mass spectroscopy (GC-MS). Testing parameters are time, hold temperature, and oxygen partial pressure. In this way, different exposure scenarios and conditions could be investigated.

To simulate the thermal exposure experienced by components present in HMAs during formulation, blending, time, and hold temperature can be varied. GC analysis is basically the time separation of substances, mainly due to differences in vapor pressure. Volatile chemical compounds are brought into the gas phase and elute at different times (plotted as x-axis). The GC “count” (plotted as y-axis) is a measure of the abundance of a certain compound present in the headspace sample. Additionally, the mass spectrum is recorded for each substance to further improve compound identification. Annealing in air could give information on the potential of a material to oxidize and release oxygen-rich compounds such as aldehydes, ketones, and acids. Annealing at a single temperature for an extended period could give information on the potential of a certain material to release compounds when held in storage for a long time (at lower or ambient hold temperatures) or when held during application operations in a melt tank (at higher temperatures).

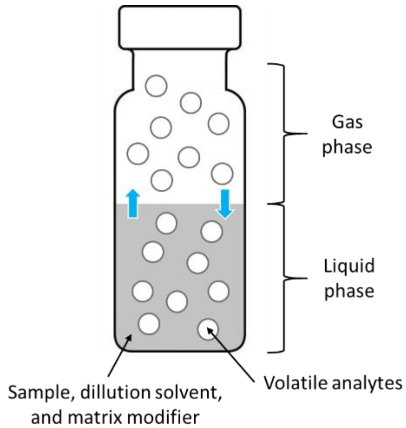

Figure 2. Schematic of a vial for headspace analysis. Volatile compounds will partition from the liquid phase into the gas phase and vice versa. By heating the sealed container, volatiles accumulate in the gas phase and could subsequently be extracted and injected onto a GC column for further analysis.

Figure 3 shows the chromatograms of the accumulated headspace vapors generated by three hydrocarbon tackifiers — designated T5, T6, and T7 — incubated in a sealed vial (0.2 g in 20 mL) at a hold temperature of 210°C for 30 minutes. Under these conditions, the thermal exposure experienced by components of HMAs during the blending operation, normally carried out without nitrogen blanketing at elevated temperatures, is simulated. From Figure 3, it is clear that sample T6 (a commercial partially hydrogenated resin) has a significantly higher level of volatile chemical compounds than both developmental partially hydrogenated resins T5 or T7. By combining gas chromatography with mass spectrometry, even more information is generated and individual chemical compounds could be characterized further. By systematically changing each of the three important parameters — time, hold temperature, and oxygen partial pressure — the accumulated collection of volatile compounds in the gas phase gives different information under varying conditions (vide supra). Annealing under aerobic conditions gives data on possible oxidation, releasing oxygen-rich compounds such as aldehydes, ketones, and acids that could be detected and analyzed. On the other hand, prolonged storage and manufacturing conditions could be simulated, giving more information on the stability of the adhesive constituent in various situations.

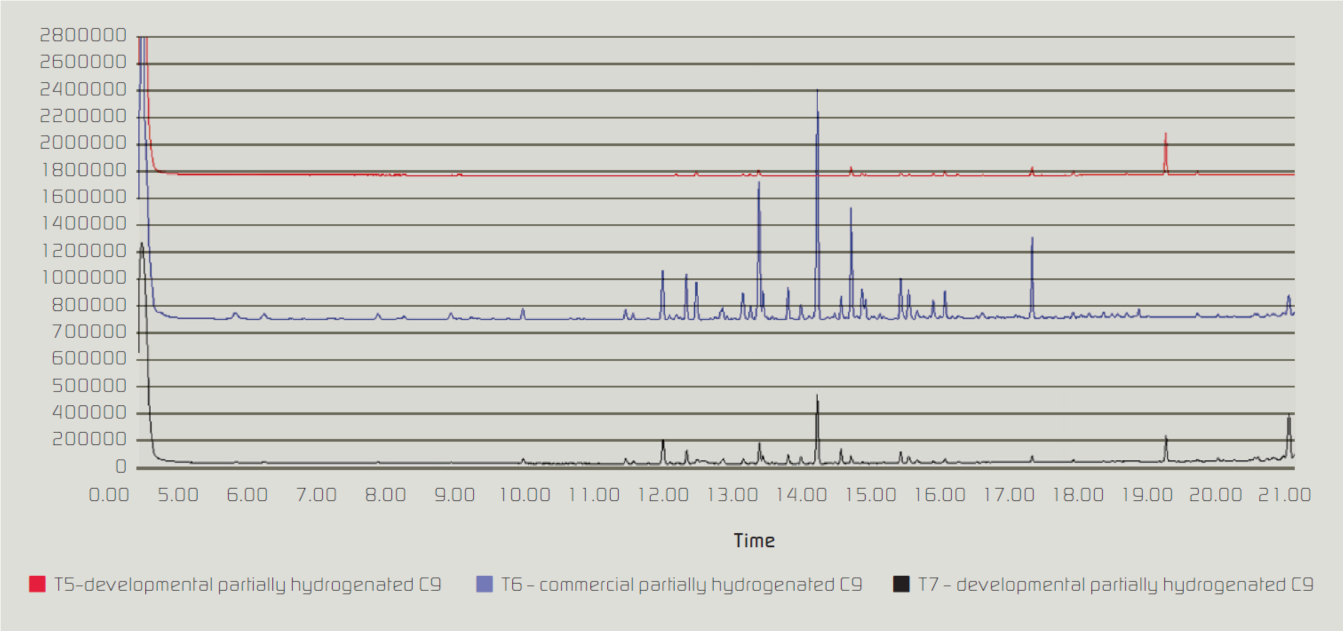

Figure 3. Headspace GC-MS chromatograms for three hydrocarbon tackifiers [2]. Sample T6 (a commercial partially hydrogenated C9 hydrocarbon resin) has significant higher levels of volatile compounds compared to both developmental partially hydrogenated C9 hydrocarbon resins, T5 and T7.

The annealing temperature is an especially critical variable. By elevating the hold temperature, both the number of different compounds and the total amount released are greatly increased. In one typical headspace GC-MS experiment, a comparison was made between a partially hydrogenated tackifier heated inside a sealed vial for 30 minutes at a hold temperature of 120°C and another at a hold temperature of 210°C. In Figure 3, the difference in the amount and intensity of volatile compounds is clearly visible. The upper scan (held at 210°C) shows a dramatic increase in number of peaks, corresponding to many more substances in the range of 6–10 carbon atoms released than for the material held at 120°C (lower scan). Furthermore, the overall GC peak area of the various volatiles, corresponding to the amount of a specific compound present in a sample, was significantly higher for material held at 210°C than the area for the same peaks from material held at 120°C. For example, the area of the peak at 11.3 minutes in the chromatograph obtained at 210°C is 18 times higher than the area count of the same peak in the chromatograph obtained at 120°C for the same material. Elevated temperatures affect complex organic materials such as tackifiers, polymers, and adhesives even when containing antioxidants and other stabilizers to improve heat stability. By choosing the correct experimental parameters, a wealth of information can be gained under a wide variety of conditions. In general, a headspace GC-MS method run at 120°C or lower provides information on volatiles contained in HMAs and their raw materials that might become volatile at storage and use temperatures. The method run at 150°–250°C provides information about volatiles released or generated during formulation blending and product manufacturing conditions.

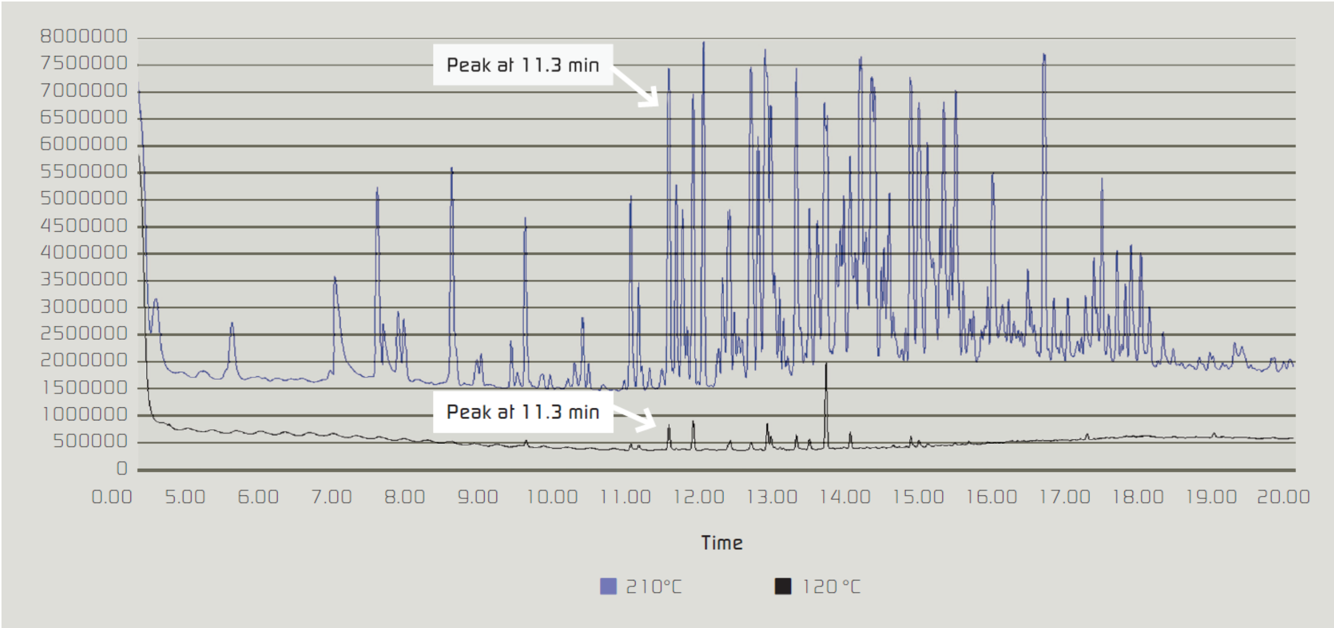

Figure 4. Headspace GC-MS results of samples treated at different temperatures [2]. Upper scan shows a method run at 210°C, while the lower scan shows a method run at 120°C.

GC-MS sniffing

Chemical information obtained with the GC-MS headspace method is often useful for odor assessment, yet it also has its limitations. GC sniffing is a powerful technique that combines the chemical information typically gained from gas chromatography with the sensory information provided by the chemical receptors in the human olfactory nerve system. In fact, the combination of chemical and olfactory information creates the most powerful tool possible for the characterization and identification of odors. In GC sniffing or GC-olfactory (GC-O) detection, part of a GC gas flow is transferred to the nose of a trained panelist via a sniffing port. By combining the responses of a chemical detector with those of a GC sniffing panelist, each individual odor-relevant substance could be detected and identified with the odor character and intensity described and ranked by the panelist to generate a sensory profile. In other words, GC sniffing enables the determination of chemical compounds that smell and what they smell like. In addition, it also identifies chemical compounds that do not smell. Typically, the result of GC-MS sniffing is a sensory odor profile in combination with the chemical identification of the components. When generating the overall sensory profile, odor characteristics such as “burnt”, “chemical,” “fatty,” “green,” “moldy/earthy,” “petroleum-like,” “plastic,” “solvent-like,” and “sweet” are considered.

The sensory profile depicted in Figure 5 shows significantly improved odor profiles of two developmental samples (T1 Dev and T2 Dev) compared to the standard resin (P1). The intensity and the type of odor have been determined by means of GC-MS sniffing. The samples have been aged at 160°C for 4 hours to simulate the aging conditions of HMA processing. The developmental sample T2 Dev has an extremely good odor sensory profile in all odor directions.

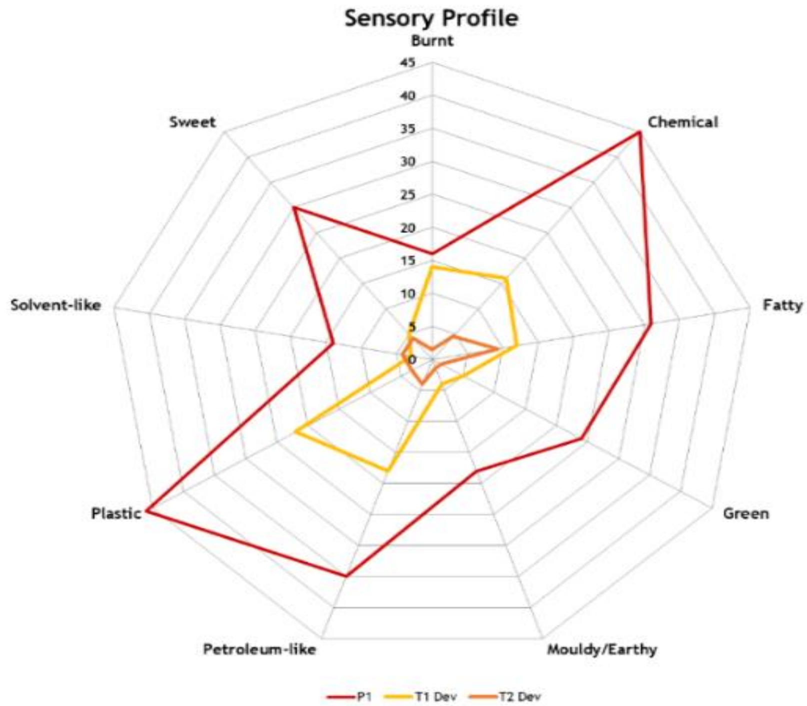

Figure 5. Sensory plot of a regular partially hydrogenated sample *versus* two developmental samples T1 Dev and T2 Dev, respectively. Both resins were aged at 160°C for 4 hours and compared to the standard resin (P1). Volatiles were trapped and analyzed by means of GC-MS sniffing. Both developmental samples and especially T2 Dev shows a low-odor sensory profile in all odor directions.

Odor panel testing

As mentioned earlier, odor perception is easily associated with concerns on potential negative health effects. With this in mind, the human nose is the obvious choice for evaluating the odor character of current and developmental products. The method of choice to conduct such an evaluation is by using an odor panel. Therefore, odor panel testing of tackifiers was conducted following the methodology used by HMA applicators [6]. Each odor panel consisted of 5–10 volunteer participants. The trial area was quiet and free of extraneous odor distractions. The number of trials on a given day was limited to no more than four samples to avoid inducing participant sensory fatigue or anosmia. Test samples were aged at 160°C for 4 hours in aluminum foil-covered glass jars immediately or cooled to certain temperatures to simulate adhesive production process conditions prior to the panel trial. Since odors that might be described as “chemical,” “solvent,” “plastic,” and “petroleum-like” could raise particular concerns, panel participants were asked to focus on odor character and intensity and report for each sample how strongly unpleasant and/or “chemical” it was perceived. The result for each person for a given sample was a single numerical ranking or rating. The total of a sample’s ratings or rankings constituted its score. In Table 1, testing results for four hydrocarbon tackifiers as assessed by the odor panel are displayed. In this trial, the panel perceived the most unpleasant odor for tackifier T2, while tackifiers T1, T3, and T4 were less odorous than tackifier T2. Furthermore, no real significant difference in odor perception was observed between tackifier T1, T3, and T4.

Table 1. Odor panel testing results for four hydrocarbon tackifiers [2]

Participant	T1	T2	T3	T4
1	1	3	4	2
2	1	2	3	4
3	4	2	3	1
4	2	4	1	3
5	3	4	1	2
SCORE	**11**	**15**	**12**	**12**

Even though odor panel testing may be the best and most direct way to understand the experience of an adhesive applicator, a formulator, or product end consumer, it does come with some limitations and errors:

(1) Safety concerns — Certain hazardous substances are not appropriate for testing through odor panels. The level of VOCs should first be confirmed safe by analytical methods, such as headspace GC-MS.
(2) Anosmia or sensory fatigue — No more than four samples on a given day could be evaluated by any individual before sensory fatigue sets in. In fact, the human nose becomes rapidly used to the odor, and this will result in a decrease in perception.
(3) Only relative — Without rigorous panelist training and standardization, the odor panel approach provides only a ranking of closely related samples of similar materials, not an absolute, quantifiable measure of odor.
(4) No identification — Identifying VOC-causing odors in odor panel testing is very difficult if not impossible.

Complex relationship between odor and VOCs

A link exists between VOCs, as a generally defined group, and odor as perceived by a consumer or end user [2]. Nonetheless, trying to quantify that link is extremely difficult because the individual volatile organic compounds vary widely in their olfactory intensity (i.e., their ability to stimulate the perception of odor) and sensory quality (pleasantness *versus* unpleasantness). As mentioned above, different odor characteristics receive different odor perceptions. Determining the most odor-questionable or malodorous compounds present in a certain product, measuring their concentrations, and identifying their source are effective controls of the overall odor perception. In fact, controlling the generation and emission of these specific compounds is more important to odor control in a final product than overall VOC concentration.

A relationship was found between odor panel trial results for hydrogenated hydrocarbon tackifiers and the levels of certain compounds released and/or generated in them during headspace GC-MS testing. Figure 6 shows odor trend and volatiles levels determined by headspace GC-MS, where four different partially hydrogenated hydrocarbon tackifiers (T6, T7, T8, and T9) were incubated at 160°C for 4 hours. First, panelists ranked odor levels for these four tackifiers from highest to lowest. In consecutive order, the lowest perceived odor was for tackifier T6, followed by tackifier T7 and T8. Tackifier T9 was perceived with having the highest odor level. Subsequently, the headspace GC-MS analysis provided a quantitative measure of three types of volatiles (aromatic, oxidized, and saturated) released at 160°C over a 4-hour annealing cycle. The total volatile level of tackifier T9 was determined to be the highest, yet it had the mildest odor. Tackifier T8, which also did well in odor performance, had the highest level of oxidized organics. From the presented data in Figure 6, it is shown that the concentration of aromatic species is the most important predictor of odor performance, with Tackifier T6 having the highest aromatic level and the poorest odor performance, while tackifier T9 has the lowest aromatics level and the best odor performance.

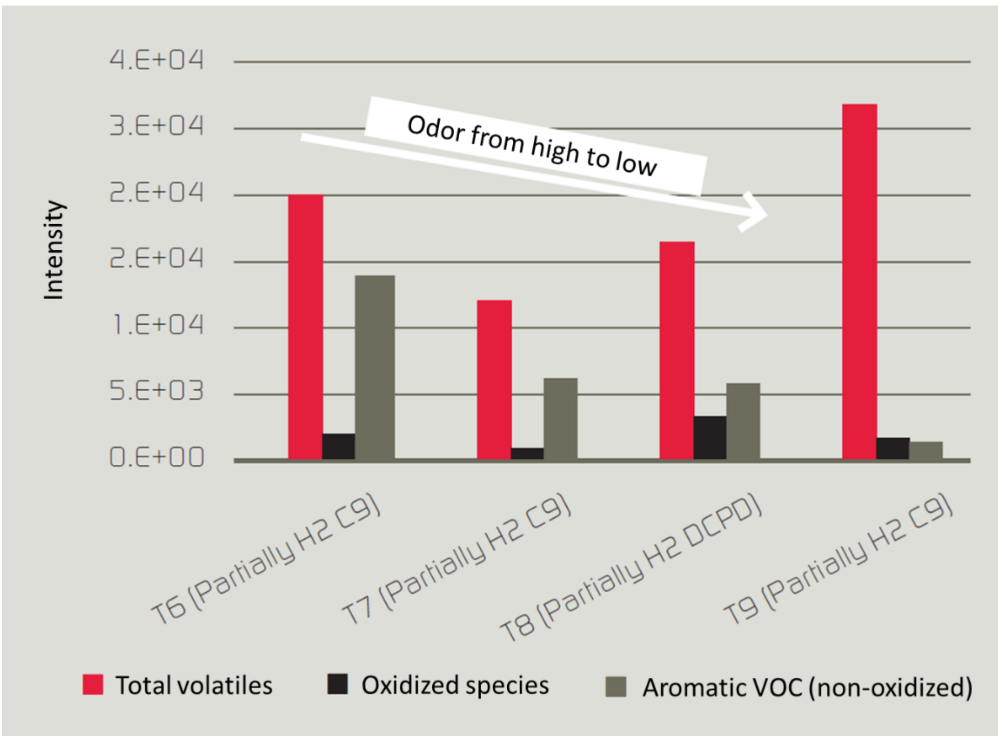

Figure 6. A comparison of four hydrogenated hydrocarbon tackifiers (T6, T7, T8, and T9). In consecutive order, the perceived odor by odor panelists from high to low is Tackifier T6 (highest), T7, T8, and T9 (lowest) [2].

Conclusion and final remarks

For application and product development, there is an increasing need for low-odor and low-VOC raw materials. Nonetheless, the relationship between both odor and the volatility of chemical compounds is very complex.

For odor evaluation and VOC determination, olfactory measurements and new analytical techniques have been developed to determine, characterize, and measure the odor and VOC content of a final product. In this regard, combined GC-MS headspace analysis, GC sniffing, or GC-olfactory detection and odor panels with sensory profiling have proved to be powerful tools.

Even though odor panel testing may be the best and most direct way to understand a particular odor experience, it does come with some limitations and errors, such as certain safety concerns, sensory fatigue, and lack of quantifiability and compound identification. Odor panel testing provides only limited and relative information on the volatile substances contained in or generated by a tackifier, polymer, or adhesive.

A relationship was found between odor panel trial results for hydrogenated hydrocarbon tackifiers and the levels of certain compounds released or/and generated in them during headspace GC-MS testing. It was shown that the concentration of aromatic species is the most important predictor of odor performance.

In summary, odor intensity is related to the amount of specific types of volatile organic compounds that are released as measured by headspace GC-MS. Perception is controlled by constituent volatiles that have both a low odor threshold and unpleasant sensory character, not by the total amount of volatile substance. Reducing or eliminating odor-generating species, either as residuals in raw materials or as generated by downstream processes, is a potentially effective strategy for improving the perception of the quality and safety of an adhesive product.

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