SYNTHESIS OF GEL AIR FRESHENER AND ITS STABILITY

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT: Fragrance compounds have been used since antiquity to freshen the air or to mask the odours. Different types of air fresheners are known such as electric air fresheners with 30% market share, sprays, including aerosol air fresheners with 27%, car air fresheners with 16%, gel air fresheners with 9%, candle air fresheners and wax melts with 7 %, liquid air fresheners with 6% and others. According to research studies, in the United States, 34.7% of the population reported health problems, such as migraine headaches and respiratory problems, when exposed to fragranced products. Thus, there are numerous studies with strong evidence that fragmented products can trigger adverse health effects in the general population. Considering that air fresheners have been associated with adverse negative health effects that was the motive for proposing an alternative way of synthesis of gel air fresheners that is more green and more healthy. In this paper the gel air fresheners were synthesized by a simple and green sol-gel reaction using natural biodegradable polymer gelatin and lavender essential oil, as well as with natural banana aroma. The 3D structures of gel air fresheners of desired shapes and odours were obtained. The change in the 3D structure at room temperature was evident, probably as a result of thermal degradation and water evaporation. Anyway, the gel air freshener obtained with lavender essential oil is more acceptable to human health than commercially available ones. The results obtained in this study suggest that further improvement in stability should take place.

KEYWORDS: gel air freshener, synthesis, gelatin, lavender essential oil, natural banana aroma, health impact

INTRODUCTION

Fragrance compounds have been used since antiquity to fresh air and mask odours. For example, the ancient Egyptians were known to use musks and other natural materials to scent their tombs. Over the last 2,000 years a variety of compounds, including numerous spices and floral extracts, have been used for their ability to impart a pleasant aroma. However, the first modern air freshener was introduced in 1948. This product, using technology developed by the military to dispense insecticides, was a pressurized spray containing about 1% perfume, 24% alcohol or other solvents, and 75% chlorofluorocarbon (CFC) propellant.This was able to deliver a fine mist of fragrance that remained suspended in the air for a long period of time. This format of the product became the standard in the industry and sales grew tremendously. In the early 1950s, many companies began to add odour-counter-act ant chemicals to their formulas. These were chemicals that were intended to actually destroy or neutralize offensive odours, as opposed to simply masking them with fragrance. Perfumery houses showed these active chemicals were capable of reducing a variety of unpleasant odours, such as cigarette smoke, urine and faecal odours, cooking smells, and amine odours typically associated with fish. Compounds used for this purpose included various unsaturated esters, long-chain aldehydes and a few pre-polymers. In modern society, nearly all the people are familiar with air freshener. Air freshener is made from two major components. The first component is deodorant, which generally includes propellants, condensed gases, and substances which can have chemical reaction with sulphur compounds, ammonia, amines, formaldehyde, such as ferrous sulphate.

And the second component is freshener, which generally includes polyols, peppermint oil, essence and other substances.

In the last 25 years, aerosol air freshener formulas were modified to improve performance and reduce formula costs. The market significantly shifted away from aerosols, due to concerns about destruction of the ozone layer by chlorofluoro-carbons (CFCs).

While reformulation by the aerosol industry has kept this product form from disappearing completely, alternate air freshener delivery forms have become increasingly popular. In the 1990s, a resurgence in potpourri and candles lead to a host of new air freshening products. For example, Kalib Enterprises Ltd.'s Potpourri (Figure 1), which contains a blend of dry spices and herbs, uses a battery-operated fan to circulate fragrance throughout the room.

Figure 1. Potpourri packet [1].

Arizona Natural Resources Inc.'s Crystal Candle division has introduced candles that kill odours, as well as aromatherapy candles that have specific therapeutic uses.

One of the most innovative, and popular, new formats is Glade Plug-Ins, manufactured by S. C. Johnson of Racine, Wisconsin. By the late 1990s, sales of air fresheners in the United States had exceeded several hundred million dollars per year. One the most successful new products are Glade Plug-Ins (Figure 2), which use heat generated by electric current to vaporize air-freshening ingredients. It consists of a tiny plastic tray containing a gel-like fragrance concentrate.

Figure 2. Glade Plug-Ins fragrance. [2]

The consumer simply peels a multilayer barrier film from the top of the tray, leaving a permanent membrane layer that allows the fragrance to diffuse into the air. The tray is inserted into a warmer unit, which then is plugged into an electrical outlet. As the warmer unit heats up, fragrance permeates at a controlled rate through the film membrane, dispersing into the air [3].

The home air freshening sector is a multi-billion dollar industry, which isn't hard to believe given the staggeringly high number of air freshening devices available to consumers these days. From aerosols, sprays, and candles, to plug-ins, oils, time releasers, each with dozens of different scents to choose from, the options are overwhelming.

Getting a fresh and graceful fragrance is very important as soon as the brain receives smells there will be immediate memories and invocation create some distressing mood.

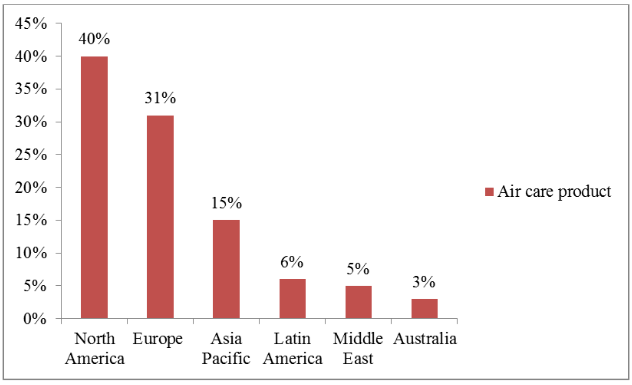

Figure 3. The worldwide representation of air care products

Air care product is a category which accounts for **9.5 billion USD globally (2016)**: North America – 40%, Europe 31%, Asia Pacific 15%, Latin America 6%, Middle East 5% and Australia 3% [4] (Figure 3). There are many different formats of air care products.

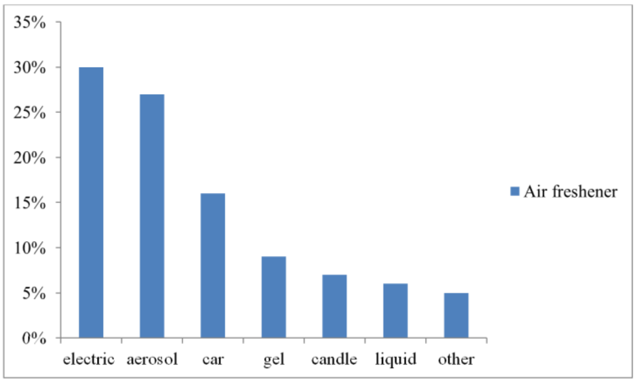

Figure 3. Different types of air fresheners

In figure 4 the percent of different types of air fresheners are shown. Electric air fresheners with 30% market share, now are fast growing because of increasing popularity of ultrasonic diffusers with some natural essential oils for this format. Sprays, including aerosol air fresheners 27% where we can observe growing importance of non-aerosol air fresheners and odour neutralizers. Car air fresheners with 16% share where especially new solid solutions launched. Gel air fresheners – 9%, stable product with very good perspective in Asia where Indian market is the most important for category. Candle air fresheners and wax melts with 7%, where wax melts products are very popular in North America and gaining popularity in Europe and Asia Pacific. Liquid air fresheners with 6% are the category with time-honoured clients. Other category is about 5%. [4]

According to one survey, the most popular reason to use air fresheners is because users like the fragrance with response of 51% of answers. The next important reason to use air freshener is refreshing the air in room with 44%. Also, to create specific atmosphere with 28% and to connect functionality of air freshener as a decorative item in house.

Even 52% do not use air fresheners and the most common reason is preference to open the window. Second important reason not to use air fresheners is because the fragrances are too strong with 31% and conviction that these products are not environmentally friendly with 23%. For 20% air fresheners are expensive, while 18% argues that air fresheners are not good for health [4].

1.1 Health impacts

Frequent use of aerosols and air fresheners in the home may make babies and pregnant women ill. British researchers have found that chemicals in these products could be linked to headaches and depression in mothers, and to ear infections and diarrhoea in babies. Aerosols and air fresheners contain dozens of volatile organic compounds (VOCs) such as xylene, ketones and aldehydes, which can be toxic in high doses. VOCs are compounds with a low boiling point that form gas or vapour at room temperature. This make them excellent scent dispersal agent. Unfortunately, aerosols and air fresheners have been linked to an increased risk of asthma, particularly in children [5].

Britain is the biggest producer and user of aerosols in Europe, with the average British household buying 36 aerosol spray cans a year. In a survey of 14,000 pregnant women, epidemiologists at the University of Bristol found that those who used aerosols and air fresheners most days suffered 25 % more headaches than those who used them less than once a week. There was also a 19 % increase in postnatal depression among women who frequently used air fresheners. The study, which was presented at an international conference on indoor air pollution in Edinburgh, found that babies under six months old who were exposed on most days to air fresheners had 30 % more ear infections than those exposed less than once a week. There was also a 22 % increase in diarrhoea among babies frequently exposed to aerosols. The biological mechanisms by which the chemicals may make people more susceptible to diseases still need to be worked out. However, experiments on mice suggest that the chemicals in air fresheners may weaken the body's defences by making the skin more permeable. A study in the US, also reported that mice exposed to VOCs from a solid air freshener experienced breathing difficulties. Rosalind Anderson from Anderson Laboratories, a private research facility in Vermont, believes that humans could be similarly affected.

According to Steinemann [6] research, who has extensively studied the health impacts of fragranced household products, one-quarter of the ingredients in air fresheners are classified as toxic or hazardous. Steinemann [6] also studied the multiple dimensions of exposures related to fragranced products and effects in the US population. 34.7 % of the population reported health problems, such as migraine headaches and respiratory difficulties, when exposed to fragranced products. Further, 15.1 % have lost workdays or a job due to fragranced product exposure in the workplace. Also, 20.2 % would enter a business but then leave as quickly as possible if they smell air fresheners or some fragranced product. Over 50% of the population would prefer that workplaces, health care facilities and professionals, hotels, and airplanes were fragrance-free. While prior research found that common fragranced products, even those called green and organic, emitted hazardous air pollutants, more than two thirds of the population were not aware of this, and over 60% would not continue to use a fragranced product if they knew it emitted such pollutants. Results from this study provide strong evidence that fragranced products can trigger adverse health effects in the general population. The study also indicates that reducing exposure to fragranced products, such as through fragrance-free policies, can provide cost-effective and relatively simple ways to reduce risks and improve air quality and health.

1.2 Toxicity of chemical ingredients in air commercial fresheners

In 2010, the International Fragrance Association released a master list of over 3,100 chemicals that are used by most manufacturers. Chemicals on that list include carcinogens like *p*-dichlorobenzene and styrene oxide, endocrine disruptors like galaxolide and tonalide, reproductive toxicants like phthalates, problematic disinfectants like triclosan and ammonium quaternary compounds, and numerous allergens. A fragrance can be made up of more than 100 chemicals and could include any of those harmful chemicals.

The Natural Resources Defence Council (NRDC) conducted the research and reveal that 86% of air fresheners tested contained phthalates. Phthalates are versatile chemicals, used as solvents in perfumes and fragrances, as softeners in plastics, as anti-foam agents in aerosols, and as sealants and adhesives. Given their many uses, phthalates are found in a wide array of consumer products, including cosmetics and fragrances, pesticides, pharmaceuticals, vinyl children’s toys, automobiles, paints, and interior finishes. Phthalates are used in air fresheners to dissolve and carry the smell of fragrances. When people use air fresheners, the phthalates are released into the air. They may then be inhaled, or the aerosol particles may land on the skin and be absorbed. Unfortunately, the rise in popularity of air fresheners has outpaced awareness of the potential health threats from exposure to the chemicals they may contain. Most phthalates are well known to interfere with production of the male hormone, testosterone, and have been associated with reproductive abnormalities. Numerous animal studies have linked prenatal exposure to certain phthalates with decreases in testosterone, malformations of the genitalia, and reduced sperm production [7].

Even if phthalates are found not to be highly carcinogenic in humans, however, the UK’s Public Health Centre for Radiation, Chemical and Environmental Hazards has revealed that air fresheners typically contain formaldehyde which is toxic compound.

The lowest concentration reported to cause sensory irritation of the eyes in humans is 0.36 mg/m^3 for four hours. Increases in eye blink frequency and conjunctival redness appear at 0.6 mg/m^3, which are considered equal to the no observed adverse effect level (NOAEL). A short-term (30-minute) guideline of 0.1 mg/m^3 is recommended as preventing sensory irritation in the general population. Evaluations of long-term effects, including cancer, based on a NOAEL and assessment factor approach, as well as estimates from the biologically motivated models, yield similar results, with values of approximately 0.2 mg/m^3 [8]. Formaldehyde is a well-known human carcinogen that has been definitively linked to cancers of the nose and throat. It is also known to cause ongoing irritation of the throat and airways, potentially leading to dangerous infections, frequent nosebleeds, asthma, and other respiratory ailments, reported the US government’s National Toxicology Program. These risks are particularly elevated in the elderly, infants, and people with compromised immune systems. In fact, in 2013 has been reported in the International Journal of Public Health the study of more than 2,000 pregnant women and were found that women who used plug-in air fresheners during gestation were statistically far more likely to have babies that suffered from serious lung infections.

Wolkoff and Nielsen in 2017 [9] reviewed how the four major abundant and common airborne fragrances α-pinene (APN), limonene (LIM), linalool (LIL), and eugenol (EUG) impact the perceived indoor air quality as odour annoyance, sensory irritation and sensitization in the airways. They assessed breathing and cardiovascular effects, and work performance, and the impact in the airways of ozone-initiated gas- and particle phase reactions products.

Human exposure studies with mixtures of APN and LIM and supported by animal inhalation models do not support sensitization of the airways at indoor levels by inhalation that include other selected fragrances. Human exposure studies, in general, indicate that reported lung function effects are likely due to the perception rather than toxic effects of the fragrances. In general, effects on the breathing rate and mood by exposure to the fragrances are inconclusive. The fragrances may increase the high-frequency heart rate variability, but aerosol exposure during cleaning activities may result in a reduction. Distractive effects influencing the work performance by fragrance/odour exposure are consistently reported, but their persistence over time is unknown. Mice inhalation studies indicate that LIM or its reaction mixture may possess anti-inflammatory properties. There is insufficient information that ozone-initiated reactions with APN or LIM at typical indoor levels cause airway effects in humans. Limited experimental information is available on long-term effects of ozone-initiated reaction products of APN and LIM at typical indoor levels.

1.3 An alternative way of synthesis of air fresheners

Considering that air fresheners have been associated with adverse health effects, such as migraine headaches, asthma attacks, mucosal symptoms, infant illness, and breathing difficulties, it is challenge and need to find an alternative way of synthesis more green and more healthy.

1.4 Gelatin as the main natural polymer compound in this synthesis

In this study, gelatin has been selected as the main ingredient in the recipe. Gelatin is a natural biodegradable polymer. Gelatin, one of the most versatile, naturally occurring biopolymers, is widely used in food products and pharmaceutical dosage forms. Gelatin is composed of 50.5% carbon, 6.8% hydrogen, 17% nitrogen and 25.2% oxygen [10]. Gelatin is an animal protein prepared by the partial hydrolysis of collagen which is fibrous insoluble protein, isolated from animal skin and bones, with very dilute acid.

The rigid bar-like molecules which build collagen are arranged in fibres is interconnected by covalent bonds [11]. These molecules have three polypeptide chains arranged in a triple helix that is stabilized by hydrogen and hydrophobic bonds. The particular structure of the triple helix is due to repeating Gly-X-Y sequence (Glycine-proline-Hydroproline). Only the very short N- and C- terminal regions, called telopeptides, do not form the triple helical structure [12]. Lysine and hydroxylysine (Hyl) residues and aldehyde derivatives from them makes intra- and inter-molecular covalent crosslinks [13] which bonds hold the atoms or ions together as a compound. Gelatin is heterogeneous mixture of of α-chains (one polymer/single chain), β-chains (two α-chains covalently crosslinked) and γ-chains (three covalently crosslinked α-chains) [14] and containing between 50 – 1000 amino acids.

Typical gelatin structure is Ala-Gly-Pro-Arg-Gy-Glu-4Hyp-Gly-Pro- [15].

The triple helix of type I collagen extracted from skin and bones, as a source for gelatin, is composed of α1 (I) and one α2(I) chains, each with molecular mass ≈ 95 kD, with 1.5 nm and length ≈ 0.3μm. The triple helices are coated by a cylinder of hydration with their grooves filled with solvent molecules, and this coating maintains the collagen's conformation and mechanical properties

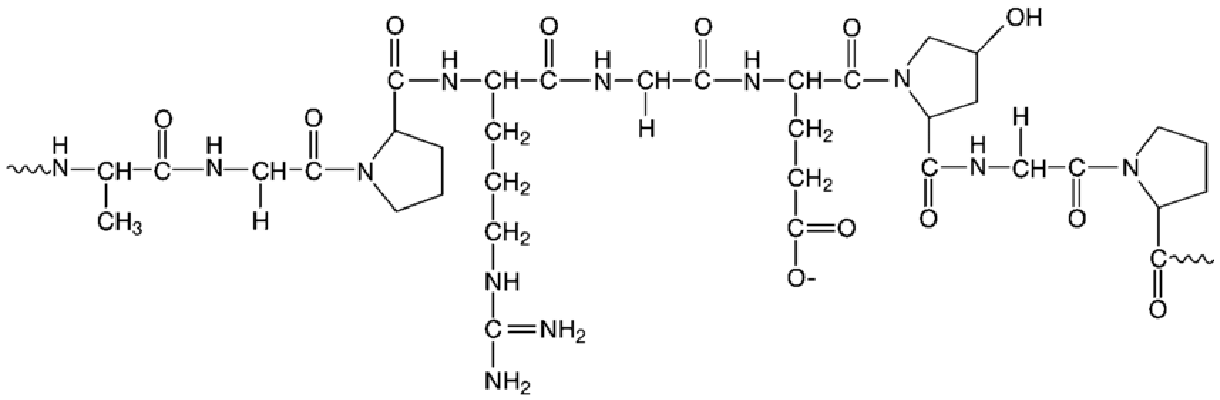

Figure 5. Chemical structure of gelatin [16]

1.5 Lavender essential oil

Lavender (*lavandula angustifolia*) is the most versatile of all essential oils. The fragrance is calming, relaxing and balancing physically and emotionally.

Figure 6. Lavender oil. [17]

MATERIAL AND METHODS

Two samples of gel air fresheners with difference in odour and colour were prepared.

2.1 Process of sol-gel synthesis

In 50 ml of distilled water at room temperature was dissolved 15 g of gelatine. 150 ml of distilled water was boiled and removed from the heat. The gelatine solution was added to the boiling water and mixed until yellow homogeneous solution was obtained. In the first sample, 15 drops of natural lavender essential oil were added, without any colour added. In the first sample 1% of the salt was also added. In the second sample 15 drops of natural banana aroma were added and yellow food colour (on the top of the teaspoon). After well stirring the homogeneous mixture was pouring into a mould with different shapes and then left in the freezer for 2 hours to cool.

After cooling in the freezer the samples were taken out at the room temperature. The 3D structures of gel air fresheners of desired shapes and odours were obtained.

RESULTS AND DISCUSSION

Prepared gel air fresheners are shown in figure 7. It is possible to note the transition from sol to gel state. The formation of gel state is observed after 2 hours of freezing. Considering that gelatin is a polyampholyte it gels below 35-40 °C. The heterogeneous nature of the molecular weight profile of this biopolymer is affected by pH and temperature, which affects the noncovalent interactions and phase behaviour of gelatin solution [18]. Marty et al. 1978 [19] first observed that the complex phase behaviour of gelatin was affected by temperature and other experimental conditions. In line with this finding, Figure 7 and 9 confirms the influence of temperature on gel structure. According to literature data, the molecular weight profile of gelatin remained unchanged at pH 5.0 to 7.0. However, at pH < 6.0, the gelatin particles lacked any net charge, resulting in aggregation at pH > 7.5; the increased charge on the particles contributed to increased resistance to dehydration.

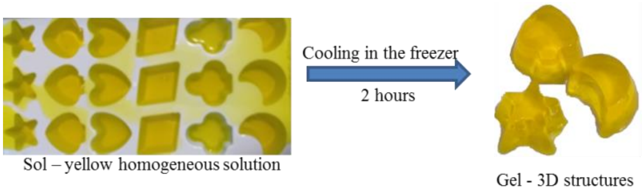

Figure 7. Sol-Gel transition and 3D structure formation.

3.1 THE TEMPERATURE INFLUENCE

At room temperature long strings of amino acids stick together in a formation called a triple matrix. This allows each chain to bond to several others, and form a complex 3D matrix. When gelatin is heated, bonds between the chains are loosen, turning the solid structure into a liquid. These gelatin chains have hydrogen atoms attached to their sides. These hydrogen branches can weakly bond with water. The oxygen atom is weakly bonded to the hydrogen atoms on the sticky-out branches of the chain. When the water receives a bit more energy by increasing the temperature, hydrogen bond will break, and the water molecule will drift away. As the water cools, it slows down until this weak bond can be re-established, linking the water to the gelatin chain again.

The stability of synthetized gel air fresheners at room temperature (around 28 °C) was studied few days. The results of the stability are shown in figure 8.

It can be observed that the 3D structure is distorted as time moves away, probably due to the loss of water by evaporation. After 84 hours at room temperature the mold starts to grow probably because of the presence of water. Knowing that tiny mold spores are all around us in the air, which is not harmful to our health in moderation. Once a spore lands on a surface, it searches for water and nutrients to feed off. Considering that mold needs water, food, suitable air quality and temperature in order to grow, this was excellent indicator that this system is not adequate and stable for the application at high temperatures. Consequently, the stability of the system synthetized has to be further improved.

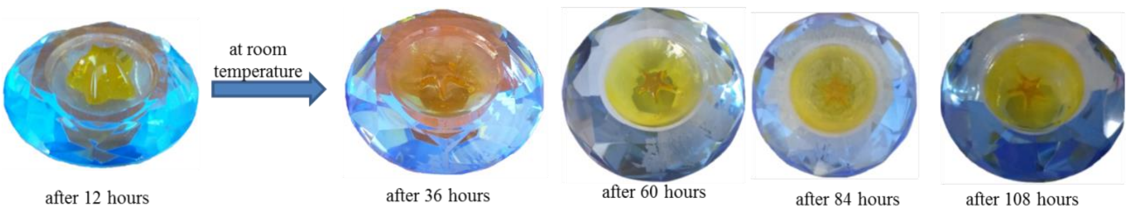

Figure 8. System stability over time.

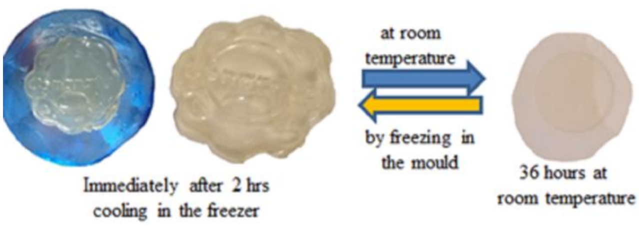

Figure 9. A reversible reaction.

It seems that the sample with lavender oil is less stable then the sample with natural banana aroma. In the figure 9 is shown that this reaction is reversible by changing the temperature.

CONCLUSION

The problem with commercially available fresheners is that they can potentially have harmful ingredients and it can be especially irritating for people with asthma and allergies. With this in mind, the challenge for this type of research was the development of new natural air fresheners with essential oils such as lavender. In this paper the gel air fresheners were synthetized by a simple and green sol-gel reaction using natural biodegradable polymer gelatin and lavender as essential oil and natural banana aroma. The 3 D structures of gel air fresheners of desired shapes and odours were obtained. The change in the 3D structure at room temperature was evident, probably as a result of thermal degradation and water evaporation. Anyway, the gel air freshener obtained in this research is more acceptable to human health than commercially available ones. The synthetized gel air fresheners in this way should be naturally anti-fungal and anti-bacterial, very effective and easy to prepare. The results obtained in this study suggest that further improvement in stability should take place.

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