

**UNDERSTANDING THE POLYMERIZATION OF ETHYL
CYANOACRYLATE IN THE SUPERGLUE FUMING OF LATENT PRINTS
TO OPTIMIZE PRINT RETRIEVAL**

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Leondra Shawntae Lawson

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ABSTRACT

The cyanoacrylate fuming method (CFM) is a widespread process used in forensics to make latent prints visible for detection, acquisition, and analysis. CFM is governed by the reaction of ethyl cyanoacrylate (ECA) with biological components in fingerprints, which serve as initiators for this anionic polymerization. CFM is not a well-controlled polymerization and there are different outcomes that may result from lower temperature, one of which fits the generalization of creating more ion-pair initiators. Another effect could be minimizing termination through suppressing side reactions. Alternatively, when paired with humidity, lower temperatures may cause surface condensation, decreasing the quality of the print. This work encompasses experiments in which fingerprints on glass undergo the CFM while simultaneously controlling surface temperatures and relative humidity to prevent quality degradation. The resulting fingerprints were assessed by direct mass measurements and the molecular weight analysis via gel permeation chromatography (GPC). This provides insight into the coupling effects of temperature and humidity on the cyanoacrylate fuming method at the molecular level in order to design a more effective quantitative and qualitative protocol for forensic scientists for the retrieval of latent prints.

Post-treatment of fingerprints to increase contrast between the fumed print and the surface of deposition has led to the introduction of different ECA formulations. One of interest is Lumicyano which combines ECA with a fluorescent powder before fuming, decreasing the need for additional steps post-fuming which saves overall processing time of evidence. Lumicyano and Sirchie ECA (“unmodified ECA”) were used to perform CFM

with different methodologies, altering surface temperature and fuming time in order to assess any variation in polymeric properties based on formulation.

A plethora of surfaces can be encountered at crime scenes. The surface of fingerprint deposition can alter the procession of polymerization through the interactions with components of the deposited print or through the behavior of the surface itself could alter CFM results. Our research investigated the changes in PECA grown on fingerprints deposited on glass, poly(ethylene terephthalate) (PET), and brass to explain how fuming on glass, plastic, and metal affect the resultant polymer and consequently, the ideal parameters for fingerprint visualization.

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CHAPTER 1 : INTRODUCTION

The Importance of Fingerprints

One of the most trusted types of physical evidence which can be obtained from a crime scene is fingerprints. Fingerprints are unique in that no two people have the same fingerprint details, including identical twins, making it advantageous in scenarios in which there are individuals with very similar DNA profiles in question for a case or crime. Fingerprints are derived from the volar pad, the flesh which allows gripping surfaces.² When endogenous compounds, internal compounds native to the fingerprint region, are secreted through the ridges of the volar pad, impressions are made.³ Impressions or fingerprints can also result when fingers encounter exogenous compounds or external contaminants, such as ink or grease.³ Fingerprints which can be seen with the naked eye, such as those caused by someone with paint on their hands are “patent fingerprints” . Those which cannot be seen with the naked eye, such as those caused by sweat, are considered “latent fingerprints”.

In order to understand retrieval methods for fingerprints, it is essential to know the components of fingerprint deposits. There are a variety of components found in a human fingerprint, some of which include eccrine sweat, sebum secretions, and water. Eccrine sweat, always present in fingerprints, is composed of a mixture of inorganic compounds (i.e. NaCl) and water-soluble organic compounds such as urea and amino acids. Sebum secretions originate from oily areas of the body, such as the surfaces of the face and head, and include fat-soluble compounds such as glycerides, fatty acids, squalene (a precursor to steroids), sterols, etc.⁴

Weyermann et al⁵ studied the composition of deposited prints using gas chromatography mass spectrometry. In this study, the temperature and humidity were not controlled but ranged between 20 – 25 °C and 40 – 80% relative humidity (RH). All deposited prints initially included cholesterol, squalene, fatty acids, steroid precursors, and wax esters. Excluding contamination from skin lotions and perfumes, the most prominent component was squalene. The change in the composition of the prints with aging was also examined, focusing on the sebaceous components of the latent print. The study shows that a major sebaceous component, squalene, nearly disappears within three days of print deposition, while the other substituents remain at similar concentrations over time.

Heat, light, moisture, and the progression of time contribute to the aging of latent fingerprints. Aging of a print usually results in a decrease in the quality of print obtained, where the loss of water appears to be important. Of the aging factors mentioned, Nixon et al.⁶ found moisture to be the most significant in the degradation of latent prints. Light was found to speed the degradation of the print but according to their results, the temperature of the aging process played no significant role in the quality of a recovered aged print. Mong, Petersen and Clauss⁷ also examined the constituents of fingermarks and the changes that occur to the components during aging. This study utilized chromatographic methods to show that with aging, the components in the fingermark residue, such as squalene, oleic, and palmitoleic acid, undergo degradation processes that shorten and oxidize these compounds. Their findings also found an 85% loss in the fingermarks weight over two weeks, which the researchers attributed to moisture loss.

There are a variety of methods utilized by forensic scientists and crime scene investigators to visualize latent prints. The method utilized must take into consideration the factors indicated in Figure 1-1, such as the substrate nature (nonporous, etc.), environmental conditions, and any other aging factors which alter the composition of the deposited print.⁸ The most basic nondestructive method for revealing fingerprints is the use of white light. When white light strikes a surface a certain angle, it can reveal the presence of a print. It is strongly advised that this method be implemented before the use of any other visualization technique.⁹ A common issue which arises in using light to reveal fingerprints is that it is difficult on highly reflective surfaces such as shiny, polished metals or glass.¹⁰

Certain contributors to the chemical makeup of the fingerprint naturally fluoresce when a laser or alternate light source is introduced. Observation of component fluorescence usually involves a filter to selectively interrogate targeted wavelengths of light and to inhibit the reflection of the incident light. This method can be implemented in a dark room before, after, or in lieu of physical or chemical processing, is safe for all surfaces, and is non-destructible.^{9, 10}

Fingerprint dusting is another popular method of revealing latent fingerprints on nonporous evidence at crime scenes and/or in a forensic lab. The process involves the use of fingerprint powder and a brush whose bristles can range from fiberglass to camel hair. Powder is applied to a nonporous surface and the brush is used to gently spread the powder on the surface to reveal prints. The fingerprints powders can vary in color to provide contrast from different colored surfaces, creating stark contrast between the

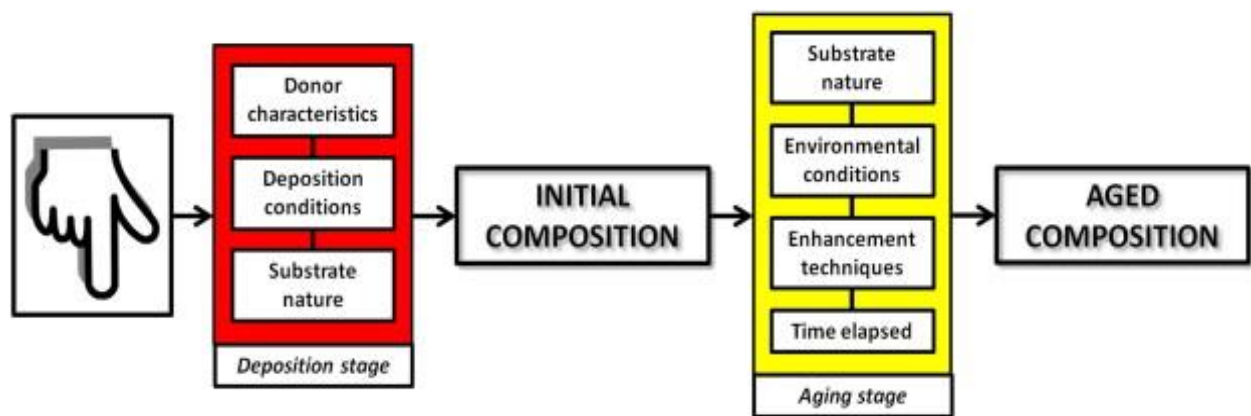


Figure 1-1: Factors affecting fingerprint acquisition

fingerprint and its deposited surface. Some fingerprint powders are fluorescent and luminate under specific wavelengths, aiding the visualization of prints on reflective surfaces. Although dusting is among the most utilized methods of latent print visualization, it has a few drawbacks. Fingerprint dusting can cause loss of detail in the final fingerprint due to damage of the print by the brush used to distribute powder on the surface. The brush may also introduce cross contamination if dusting more than one surface of a crime scene or if fingerprints from multiple individuals is present.¹⁰ Additionally, the chemical composition of fingerprint powder may degrade DNA, thus negatively affecting post-dusting analysis for the presence of DNA.^{10, 11}

Iodine fuming heats iodine crystals to allow iodine vapors to interact with grease and oil from fingerprints on porous surfaces such as paper. Evidence fumed with iodine has a yellow to brown hue and must be photographed immediately following fuming due to the swift fading of the iodine.⁹ Ninhydrin is a solution which interacts with the amino acid constituents of fingerprint residue. The use of ninhydrin to develop latent fingerprints is intended for porous surfaces and must completely dry before humidity and heat are applied to reveal the fingerprint on the surface.⁹ Once revealed, the fingerprint ridges have a purple tint and can be photographed.

Vacuum metal deposition (VMD) is a highly sensitive fingerprint development method in which a thin, invisible layer of gold metal is deposited on the entirety of a non-porous, semi-porous or porous surface under vacuum followed by a thin layer of zinc under vacuum.^{10, 12} The zinc will not adhere where print residue resides because the gold seeps into the residue inhibiting the zinc from interacting with the gold.¹² Developing latent

prints by the VMD process usually results in transparent print ridges with the background covered in metallic zinc and is considered “normal development”. VMD is considered one of the most sensitive and versatile methods for latent print visualization¹² due to its ability to enhance prints that have been exposed to adverse conditions, extensively aged (as old as 20 years), and the high detail resolution it can obtain.¹³ One drawback of VMD is the occurrence of “empty prints,” when the deposition of zinc occurs on the background but not on the print ridges, so although the print area is well-defined, it is indiscernible.¹² Other drawbacks include the cost to perform in comparison to other methods as well as the ease of use and training for the method.

Cyanoacrylate Fuming Method (CFM)

Polymerization has gained interest in forensics due to its potential to effectively amplify the fingerprint ridges and thus lead to enhanced visualization of fingerprints. Alkyl-2-cyanoacrylates, such as ethyl cyanoacrylate, are among the most reactive monomers. Cyanoacrylates have great wetting and adhesive properties which is why one common term for them is “superglue”. The cyanoacrylate fuming method (CFM) is a sensitive, non-destructive visualization technique of latent prints which does not damage DNA during processing and is easy to execute. Additionally, since cyanoacrylate is commercially available and cheap, CFM is a cost-efficient method to reveal latent prints in the lab or on the scene of a crime. This is beneficial when post-processing analysis may be needed for evidence, for example, DNA testing.

Cyanoacrylate monomers can polymerize by free radical or anionic processes. Of the two avenues, anionic is more relevant to understanding the CFM due to the easy initiation and fast polymerization of cyanoacrylates by nucleophiles or weak bases such as water, amines, or alcohols. The success of this polymerization relies on the strong electron withdrawing character of the nitrile and ester groups. In the presence of a nucleophile, these groups draw upon the negative charge of the nucleophile, causing polarization of the double bond and activating the monomer to nucleophilic attack. Propagation occurs when the electron deficient monomer attaches to a growing anionic chain end. Meanwhile, the nitrile and ester substituents stabilize the negative charge of the polymer.¹⁴

The cyanoacrylate fuming method is based on the polymerization of a cyanoacrylate monomer, where ethyl-2-cyanoacrylate is the most common cyanoacrylate and is used in these studies. This method heats the cyanoacrylate, which forms vapors that interact with the components in the print, such as amino acids and others discussed above, and is thought to follow the mechanism outlined in Figure 1-2. Ideally, the cyanoacrylate forms sufficient white polymer, poly(ethyl cyanoacrylate) (PECA) on the surface of the fingerprint to make the latent print visible on the deposited surface. This provides the most detail of fingerprint ridges and structure. If too much polymer forms on the print or on the supporting surface, there is a loss of ridge detail where overdevelopment has occurred because the print is no longer discernible from the surface.¹⁵

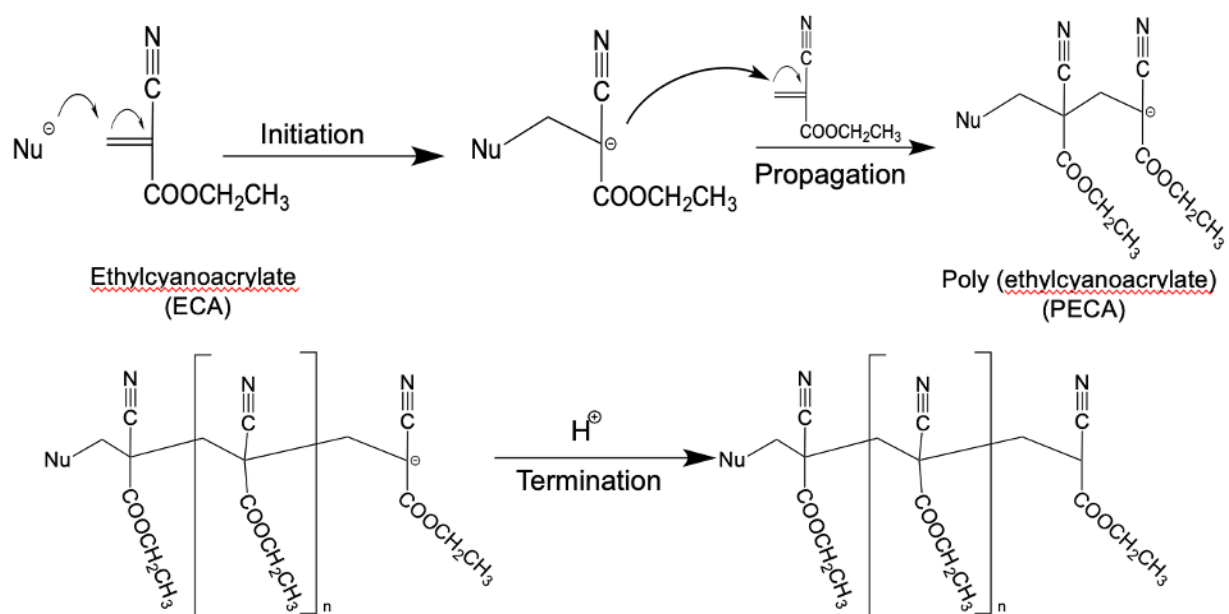


Figure 1-2: General proposed mechanism for ethyl cyanoacrylate polymerization

The CFM proceeds through the anionic polymerization of the ethyl cyanoacrylate monomer. The polymerization is initiated via constituents in the deposited prints, such as amino acids. Amino acids consist of an amine group and a carboxylate group. Wargacki et al¹⁶ studied the ability of sodium lactate, pure water or an amino acid, alanine, to initiate and grow poly(ethyl cyanoacrylate) from ethyl cyanoacrylate vapors. In these studies, the individual initiators were deposited on a stainless-steel surface and fumed under neutral, acidic, and basic pH environments. Neutral lactate accumulated PECA more quickly than water and water produced the least PECA of the three compounds tested. This was interpreted to indicate that water is not the primary initiator of the polymerization that results from the ethyl cyanoacrylate fuming.¹⁶ The amount of PECA formed from fuming the sodium lactate and alanine were very similar, indicating the polymerization occurs by similar mechanisms. This observation and further studies show that the carboxylate group is the dominant initiator of ethyl cyanoacrylate in latent fingerprints. Further studies examined the impact of exposure of aged prints to either gaseous ammonia or acetic acid immediately before the cyanoacrylate fuming method on the amount of PECA formed and the quality of the latent print. These studies showed an increase in the production of PECA on the print and provided greater ridge detail for retrieval with exposure to ammonia or acetic acid.^{17, 18} Wargacki et al¹⁹ also found that exposure of the print to air and light decreases the amount of polymer formed on the print that is developed by superglue fuming due to the loss of water. These results are interpreted to indicate that the water loss creates a local chemical environment that inhibits the growth of poly(ethyl cyanoacrylate) from the print bound initiators. This data

was then utilized to develop a methodology by which the ability of aged latent fingerprints to polymerize ECA is recovered. In this protocol, initiator was reintroduced to the system by the exposure of the aged print to the vapor of acetic acid or ammonia. These two small molecules improve the growth of the polymer from the aged print ridges by over an order of magnitude, while retaining the integrity of the print structure.¹⁶ Comparison between the two enhancement agents provides insight into the mechanism by which this enhancement occurs.

Thermal gravimetric analysis has been used to study the stability of poly(ethyl cyanoacrylate) over temperature ranging from 150 °C to 300 °C at a heating rate of 20°C/minute.¹⁴ The results of this study showed that the ethyl cyanoacrylate polymer had an initial mass loss at about 160 °C and complete loss at 300 °C. At temperatures exceeding 150 °C, the cyanoacrylate polymer “unzips” and forms smaller polymer. Due to this, cyanoacrylate fuming processes often heat the cyanoacrylate to 150 °C to form vapor that can form high molecular weight polymer.

Burns et al¹⁸ studied the effects of exposure of latent prints to vapors of basic compounds such as ammonia prior to fuming on the growth of PECA from the print when fuming with methyl, ethyl, propyl and butyl cyanoacrylate. These studies correlate the amount of cyanoacrylate polymer that was deposited during the fuming process, measured by using Fourier Transform Infrared Spectroscopy (FTIR), to the exposure to ammonia prior to fuming. The absorbance peak height of the carbonyl group served as an indication of the amount of poly cyanoacrylate formed during fuming. These FTIR peak heights correlated well with the visual quality (grade) of the prints as determined by

fingerprint experts. This result indicates that FTIR can be used to quantify the success of the development of a print by fuming, and that the exposure of a latent print to a base prior to fuming improves the quality of the developed print. Lewis et al²⁰ also examined the development of latent prints by cyanoacrylate fuming. Their findings suggest that the amount of moisture present in the print during fuming correlates to the quality of the print, the cyanoacrylate polymerization is very rapid, and the concentration of the cyanoacrylate vapors in the enclosure impacts the optimum development time.

Impact of Relative Humidity on the CFM

Ion pairs can exist in a number of states in ionic polymerizations. Figure 1-3 shows the possible arrangements of ion pairs in an anionic polymerization, which can range from a completely covalent species (I) to a completely free (and highly solvated) ion pair (IV).²¹ The intermediate species include the tight or contact ion pair (II) (also referred to as the intimate ion pair) and the solvent-separated or loose ion pair (III). The intimate ion pair has a counter-ion close to the propagating center (unseparated by solvent). The solvent-separated ion pair involves ions that are partially separated by solvent molecules. The propagating anionic chain end has a positive counter-ion.¹⁸

Increased solvent polarity favors the loose ion pair while the tight ion pair predominates in solvents of low polarity. The behavior of the ion pairs is very solvent-dependent in anionic polymerizations where the counter-ion is small, such as Na^+ , which is found in fingerprints. Free ions are much more reactive than ion pairs in anionic



Figure 1-3: Ionic behavior in polymerizations

polymerization. Therefore, the looser the ion pairs, the more reactive they become. Algaier et al.²² used the fact that increasing the size of the counter-ion formed a more loosely bound ion pair to create conditions where more poly(ethyl cyanoacrylate) is formed during fuming, but with little change to the chain length of the resultant PECA polymers.

A saturated salt solution inside a sealed environment equilibrates to a relative humidity at equilibrium. The relative humidity of this environment depends on the salt. For NaCl, found in eccrine sweat, the relative humidity is 75 percent. When the relative humidity exceeds 75 percent, the NaCl takes up water from the surrounding environment.¹² In general, it is believed in the forensic community that a relative humidity range of 70-80% leads to the most effective cyanoacrylate fuming.²³ This may be due to the solvation of ion pairs that participate in the initiation and propagation of the ECA polymerization during fuming. For instance, sodium lactate has been found to be an effective initiator for the polymerization of poly(ethyl cyanoacrylate).¹⁶ Moreover, it is known that sodium lactate dissociates into ions in the presence of moisture.¹⁵ Therefore, increased moisture is beneficial to the poly(ethyl cyanoacrylate) polymerization and will improve the mass of poly(ethyl cyanoacrylate) formed during fuming as well as the molecular weight of polymer formed by the cyanoacrylate fuming method to maintain high quality prints.

As previously stated, both eccrine and sebum secretions are excreted when a print is deposited. Paine et al studied the effect of humidity on the fuming of groomed eccrine and sebaceous prints.²⁴ For groomed eccrine prints, the average fingerprint grade

increases steadily with relative humidity up to 85%. Eccrine secretions are expected to be more affected by the change in humidity because it is primarily composed of water and water-soluble components. The developed prints obtained in this study showed marks developed at lower humidity were faint and at high humidity, large amounts of background development occurred, reducing the contrast. For sebaceous fingermarks, there was a slight increase in mark quality at 70 and 79% relative humidity, but an apparent relationship was not observed between quality and humidity. This may be due to the mucoproteins in sebaceous deposits forming a barrier that limits the incursion of water into the print and thus the impact of humidity on the CFM process of these prints. Sebaceous prints were observed to be heavily deposited and lacking in definition between ridges. It was postulated that the lack of definition was due to the smudging of the sebaceous components in the deposit as opposed to overdevelopment.

The Role of Temperature in the CFM

Control of the temperature of the CFM protocol varies based on the needs and preferences of the examiner. Heating ECA on a hot plate (or heating source) to around 80 -100 °C produces sufficient vapor to grow PECA on the print and effectively visualize latent prints.²⁵ Increasing the temperature of ECA above 220 °C can result in the emission of hydrogen cyanide, a colorless gas which alters the body's ability to use oxygen and harms the brain, heart, lungs, and blood vessels.²⁵⁻²⁸ Due to these factors, the cyanoacrylate fuming method is typically carried out between 100 °C and 200 °C. At the

midway temperature of 150 °C, the CFM appears to benefit from a faster vaporization of the ECA monomer without risk of hydrogen cyanide exposure.

The formation of ions with sufficiently long lifetimes for propagation to yield high molecular-weight products generally requires stabilization of the propagating centers. In ionic polymerizations, stabilization of reactive ion pairs may occur at lower temperatures. Relatively low or moderate temperatures also suppress side reactions that may result in chain termination or transfer, that stop the growth of the growing chain.²¹

Empirical studies have shown that the polymerization of ECA at room temperature produces the most polymer when the relative humidity is around 80 percent.²³ Previous studies have also shown that the polymerization of ECA at low temperatures and standard humidity produces a larger quantity of polymer in the fuming process.¹⁷ Steele et al²⁹ tested the fuming of ECA on a variety of surfaces and found cooling the surfaces before performing the cyanoacrylate fuming method was advantageous to the quality of the acquired prints. Decreasing the temperature led to an increase in the PECA on the surface of the fingerprints which drastically increased the ability of the researchers to detect the fingerprints on the surfaces.

A drawback to consider is that lower temperatures may cause condensation of water onto the print and surrounding surface, which can result in lower quality prints. Therefore, a more complete understanding of the combined effects of humidity and temperature on the growth of poly(ECA) on fingerprints is needed.

The Importance of ECA Formulation

It is important to take the cyanoacrylate formulation into consideration when examining the cyanoacrylate fuming process. Cyanoacrylates can have a range of viscosities. Viscosity denotes how resistant a liquid is to flow, where the viscosity is often correlated to the strength of intermolecular interactions in a liquid.³⁰ Formulations with higher viscosity tend to require more fuming time as it requires more time and/or energy to vaporize the cyanoacrylate. Alternatively, cyanoacrylates with a lower viscosity, some resembling the consistency of water, tend to vaporize more swiftly. The viscosity of cyanoacrylate tends to increase over time due to initiation of coupling reactions by moisture in the air. This in turn forms a larger compound that is harder to vaporize. Therefore, the freshness, or age, of the cyanoacrylate formulation can cause variations in the fumability of cyanoacrylate samples that are otherwise identical. As a result, these variations can require alteration in the CFM fuming time, amount of initial ECA used for fuming, or hot plate temperature in order to obtain an effective fuming process. According to Matt Schwarz of Schwarz Forensics²³, a mass reduction of 90% or more ECA monomer during fuming (difference in ECA weight pre- and post-fuming) indicates a process that balances fuming time and the amount of monomer utilized.

One concern with the cyanoacrylate fuming method is the need for the fumed print to stand out and be easily discernable from the surface after fuming. In order to increase background contrast, prints are often treated with dyes after being fumed.³¹ Lumicyano is a one-step cyanoacrylate fuming method which utilizes Lumicyano solution (ECA) mixed with a fluorescent powder. The fluorescent powder contains 3-chloro-6-ethoxy-

1,2,4,5-tetrazine. 1,2,4,5-tetrazines, also referred to as s-tetrazines, are well-studied with their resurgence in interest stemming predominantly from its optical properties such as fluorescence and electrofluorochromism. S-tetrazines have deep color ranging from purple to red in the visible spectrum and fluoresce with wavelengths from 550-590 nm, depending on the substituents on the tetrazine ring.³² Tetrazines are one of the few fluorophores that work on a $n\text{-}\pi^*$ transition.

Tetrazines react readily with a variety of nucleophiles.³³ S-tetrazines have the highest ratio of nitrogen to carbon allowed in a single ring.³⁴ As a result of the four nitrogen atoms within a six-membered ring, s-tetrazines are significantly electron deficient, have a positive quadrupole moment and high polarizability perpendicular to the ring plane.³⁵ S-tetrazines have a π^* LUMO of relatively low energy, regardless of the substituents which may be attached. This gives the s-tetrazines their red-pink-purple color. The positive quadrupole moment and high polarizability lead to the formation of anion- π and lone electron pair- π non-covalent interactions.³⁵ S-tetrazines non-covalently bond to negatively charged species, creating anion- π bonds, with unshared electron pairs (lone pair- π bonds) that reside over the ring plane near the ring centroid.³⁵ Savastano et al³⁵ evaluated the interactions between the s-tetrazine ring and electronegative atoms that contain a negative charge or lone pairs utilizing the Cambridge Structural Database (CSD). Simulations were carried out to analyze anion- π and lone pair- π interactions with s-tetrazine when in solid state and solution. The lone pair- π interactions of the s-tetrazine ring were found to be short range and weaker than van der Waals interactions in solution and the solid state. Anion- π interactions of the s-tetrazine ring were much stronger and

longer range in solid state and solution. Overall, this shows the suitability of s-tetrazine to interact with electron-rich or anionic species.

Lumicyano is intended to be used in the fuming of latent prints on semi-porous and nonporous surfaces. Lumicyano has been reported to perform better in producing visible prints than treatment of the fingerprints with the fluorescent molecule BY40 after fuming with ECA.³⁶ Groeneveld et al.³⁷ examined the inclusion of a UV active or fluorescent group into a cyanoacrylate monomer for the purpose of revealing or enhancing latent prints.³⁷ They were successful in their synthesis and compared their work to the commercially available fluorescent cyanoacrylate formulations, Polycyano UV and Lumicyano. Their “Oligocyano” had the same optical and morphological properties as the commercial products, but the Oligocyano had a different thermal behavior than Polycyano UV. Their results also suggested the polymerization of ECA in Lumicyano and Polycyano UV formulations were driven by dipole-dipole attractive forces, with no covalent bond between the fluorophore and monomer/polymer. Also, the degree of polymerization of PECA formed from both commercial fluorescent formulations were comparable to the PECA formed from the fuming of regular ethyl-2-cyanoacrylate monomer. These researchers also note that the nanofiber morphology of the PECA formed from Lumicyano offered slightly superior visibility than morphologies formed from regular cyanoacrylate. They attribute this variation to the basic nature of the fluorophore inhibiting termination of the polymerization.

Risoluti et al.³⁶ also concluded that the Lumicyano does not result in the formation of a chemical bond between the PECA polymer and fluorophore. Rather, weaker

interactions exist that are sufficiently stable to maintain some fluorescence. They also found that Lumicyano reveals fingerprints under fluorescence that are not detected by white light alone. Lumicyano also eliminates the need for post-treatment and the associated additional time needed for such analyses.

The Role of Surfaces in the CFM

There are a variety of surfaces on which prints reside that can be encountered at the scene of a crime. The chemistry of the surface may also offer additional ECA initiation sites, producing a competition between the surface and the fingerprint components in the growth of PECA. Alternatively, the surface chemistry may inhibit the initiation of polymerization. Moreover, the wettability of the surface may also impact the interaction of the fingerprint and ECA. The process of wetting is related to the surface tension of the wetting fluid and involves the adsorption of liquid molecules on the surface.³⁸ The wetting process can be assessed through evaluating the relationship of the contact angle and the surface tension, which is depicted in Figure 1-4 and represented by Young's equation (Eqn. 1):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \times \cos \theta_e \quad \text{Eqn. 1}$$

In Equation 1, γ_{SV} is the solid-vapor surface tension (mN/m), γ_{SL} is the solid-liquid surface tension (mN/m), γ_{LV} is the liquid-vapor surface tension (mN/m) and θ_e is the contact angle of the liquid at the solution interface (degrees). The contact angle quantifies

the

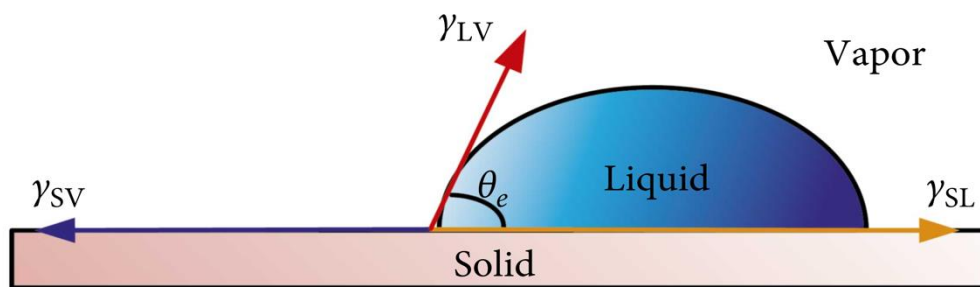


Figure 1-4: The relationship between the contact angle and the solid-liquid, solid-vapor, and liquid-vapor surface tension³²

propensity of the liquid molecules to adhere to and spread on a surface. These processes play a vital role in defining the effectiveness of the CFM to successfully polymerize ECA and produce sufficient polymer to clearly differentiate a print from its substrate.

For instance, Bond and Brady³⁹ studied the acquisition of fingerprint impressions from copper pipe bomb fragments after an explosion. They found that the increase in temperature from the explosion accelerates the corrosion of metal, especially copper, by the sodium chloride in eccrine sweat, leaving fingerprint ridge impressions in the metal. In addition to the NaCl in prints, light can impact the quality of the print obtained from a metal. Payne et al used silver electroless deposition (SED) as a visualization technique and compared it with the CFM method on brass, copper, and stainless steel.⁴⁰ Their findings showed that dark and dry conditions are ideal to develop prints on brass utilizing the CFM. When comparing the quality of print obtained from different surfaces, the CFM provided higher quality prints than SED for each surface.

Work by Steele et al showed the processing temperature for CFM varied based on surface type. Although surface temperature studies were conducted on three different surfaces, the underlying reasoning behind the need for different processing temperatures was never investigated. Despite the CFM being carried out on different surfaces, such as the work by Steele et al, the focus of previous studies has predominantly been placed on how to successfully visualize prints on different surfaces as opposed to understanding the factors which dictate the success of the ECA polymerization. We, therefore, seek to understand how the cyanoacrylate fuming method is impacted by the structure and composition of a surface on the resulting PECA polymer to provide insight into the

optimization of the CFM method for the retrieval of prints regardless of the surface of the deposited print.

Overview and Summary

In summary, anionic polymerizations at lower temperatures create more reactive ion-pair initiators and improved propagation.^{22, 41} A lower temperature may also cause condensation of water vapor from the air onto the surface, which will likely decrease print quality by either inhibiting polymer growth or allowing polymer growth outside the print ridge. Taking this into account, it is important to understand the combined impact of temperature and humidity on the fuming process in order to more fully optimize the growth of the polymer during fuming in order to aid forensic scientists in reproducibly developing better quality prints.

Evidence can be processed for latent fingerprints in the lab if the evidence is portable/small enough to take back to the lab, but there may be instances in which evidence must be processed at the crime scene. Because the conditions such as temperature, weather, etc. are not easily controlled at the scene of a crime, understanding how temperature and relative humidity affect the CFM provides insight to forensic scientist to adjust conditions when feasible to optimize the visualization of the prints under different conditions. Modifications to the ECA formulation can also cause variation in the success of the polymerization. Additionally, we seek to understand how the surface of a deposited print impacts the visualization, polymerization processes, and ultimately, the overall success of the CFM. Understanding the role of surface chemistry on the success of the

ECA polymerization during fuming offers additional insight for the forensic community to vary fuming conditions to bias the formation of quality prints on a variety of surfaces.

CHAPTER 2 : ENHANCING THE CYANOACRYLATE FUMING METHOD OF LATENT PRINTS BY OPTIMIZING SURFACE TEMPERATURE AND HUMIDITY

Abstract

The cyanoacrylate fuming method (CFM) is a widespread chemical process used in forensics to reveal latent prints on surfaces via the reaction of ethyl cyanoacrylate (ECA) with biological components that exist in fingerprints. This reaction is the polymerization of ECA, which is initiated by these biological components. The combined impact of both relative humidity and surface temperature on the growth of poly(ethyl cyanoacrylate) (PECA) from deposited fingerprints during fuming is not well understood. We report results that elucidate the combined effect of humidity and temperature on the growth of PECA from latent fingerprints on glass slides by completing the CFM in a fuming tank at different humidity levels, surface temperatures, and fuming times. The amount of PECA and its molecular weight were analyzed by monitoring the increase in mass on the surface and gel permeation chromatography (GPC), respectively.

Our results indicate a competition of effects that impact the success of the fuming process. The most favorable prints were observed at ambient relative humidity at lower temperatures, with 80% relative humidity showing an overdevelopment of prints for all temperatures tested with decreased molecular weight of the formed PECA. For all humidity levels tested, the appearance of excess water on the surface was most prominent at the lowest surface temperatures, which appeared to coincide with lower molecular weight PECA. The amount of PECA formed at ambient relative humidity (*about* 25-35% in our lab), increases with a decrease in temperature. However, the increased PECA does not always correspond to improved quality of the developed print, as too much PECA can result in an overdeveloped (visually indiscernible) print. Adjusting fuming time proved advantageous to control the overdevelopment of the print for all humidities

except 80%. Thus, decreasing print temperature at such a high humidity provides little advantage. Overall, simultaneously controlling surface temperature, humidity and fuming time offers a straightforward method to enhance the visualization of prints on glass. This holistic study, therefore, provides fundamental insight into the molecular level processes that govern the fuming process of latent prints, offers forensic scientists guidelines to further optimize procedures for the visualization of fingerprints by the CFM method, and elucidates methods to minimize overdevelopment of the prints.

Introduction

The cyanoacrylate fuming method (CFM) is used by forensic scientists to visualize latent prints on nonporous and semi-porous evidence from crime scenes. In this method, the monomer, ethyl cyanoacrylate, is heated below the evidence that contains the fingerprint and its vapors interact with the biological constituents found in prints. As these vapors interact with the latent print., the ECA polymerizes to form chains of poly (ethyl cyanoacrylate) (PECA) on the surface of the print, creating a solid on the print that enables the visualization of the print ridges.

The polymerization in the cyanoacrylate fuming method is primarily an anionic mechanism, which is strongly driven by the electron withdrawing character of the nitrile (-CN) and ethoxy carbonyl (-COOCH₂CH₃) groups of the cyanoacrylate monomer.^{14, 37, 42,}
⁴³ When a nucleophile is present, these groups withdraw electrons leading to the double bond being highly vulnerable to attack by a weak base.¹⁴ The initiation reaction and addition of the next few monomers determine the reactivity and properties of the cyanoacrylate polymer. Computational analysis of the thermochemistry of the chain propagation of ethyl cyanoacrylate by Loschen et al showed after a degree of polymerization of four or five, the reaction energies nearly converge, that is to say approaching similar reaction energy values.⁴⁴ Anionic polymerization of cyanoacrylate monomers in the presence of weak bases at ambient temperatures is highly exothermic and occurs rapidly.^{14, 44}

The polymerization requires an initiation step, where a component in the fingerprint must react with the ECA vapor to begin the polymerization reaction. There are a variety of components found in a human fingerprint, some of which are eccrine sweat, sebum

secretions, and water. Eccrine sweat, always present in fingerprints, is composed of a mixture of inorganic compounds and water-soluble organic compounds (such as NaCl, urea, and amino acids). Sebum secretions originate from oily areas of the body, such as the surfaces of the face and head, and include fat-soluble compounds such as glycerides, fatty acids, squalene (a precursor to steroids), sterols, etc.⁵

Loschen et al revealed that the initiation reaction and addition of the first few monomers determine the reactivity and properties of the PECA polymer.⁴⁴ Wargacki et al tested the ability of lactate, alanine, and water, primary components of eccrine sweat, to initiate the polymerization of ECA fumes to identify the dominant components in the print that initiate the polymerization of ethyl cyanoacrylate from a latent print. Water showed much lower amounts of polymer formed than the amino acids, verifying that water is not the primary initiator in the CFM process. These studies identify the carboxylate groups of amino acids as primarily responsible for the initiation of the polymerization and establish that a higher pH results in more polymer growth due to the reduction of potential terminating agents in the anionic polymerization.¹⁶

Czekanski et al. examined possible initiators for the anionic polymerization of cyanoacrylate utilizing small scale CFM experiments. Pure compounds (i.e. inorganic salts, fatty acids, amino acids and hydrocarbons) as well as mixtures such as cooking oil, motor oil and chicken broth were deposited in wells on slides. Deposited solutions were allowed to dry completely before fuming. These dry films did not lead to polymer formation during fuming. Therefore, the authors concluded inorganic salts and amino acids alone did not initiate the polymerization that occurs in real fingerprints. Czekanski et al did find that ECA polymerized from some alkanes, with the polymerization occurring more quickly

for smaller alkanes, suggesting that the molecular weight of the initiator affects the fuming rates.⁴³ These results therefore highlight the presence of over 58 different hydrocarbons found on the surface of the skin, and that some alkane films respond similarly to real fingerprints in the polymerization of ECA vapor.

These amino acid results of Czekanski are in contrast to the results from Wargacki et al. This difference is likely due to the fact that Czekanski et al allowed the solutions to completely dry. Although water is not the primary initiator in the polymerization, humidity is nonetheless a vital component to a successful cyanoacrylate fuming procedure. Wargacki et al found water loss creates a local chemical environment that is less suitable for the growth of poly(ethyl cyanoacrylate) from the print bound initiators.⁴⁵ These studies indicate that the humidity serves to solvate the initiators in the anionic polymerization of ethyl cyanoacrylate vapor, where its presence solvates the initiating ion pairs and therefore, increasing reactivity with increasing humidity. Algaier et al. found that increasing the size of the counter-ion formed a more solvated or loosely bound ion pair which resulted in more poly(ethyl cyanoacrylate) formed during fuming with little change to the chain length of the resultant PECA polymers.²²

Chain growth of ECA during the propagation step of polymerization occurs when the monomer attaches to the anionic chain end. Meanwhile, the electron withdrawing substituents stabilize the negative charge on the growing polymer chain end by localizing the negative charge on the α -carbon.¹⁴ Ablat et al studied the anionic polymerization of 5 types of alkyl cyanoacrylates using density functional theory (DFT) and DFT with dispersion correction (DFT-D3). The results of their simulations indicate the van der Waals forces between bound monomers have a significant impact on the stabilization of

the growing poly(cyanoacrylate) chains, with a larger effect observed in monomers with longer alkyl groups. The polymerization is shown to be exothermic for all of the alkyl cyanoacrylates tested. The simulations infer that the polymer chains are greatly stabilized by intra-chain dispersion forces with the rate of the propagation reactions becoming independent of chain length after the addition of three monomers, similar to the results obtained by Loschen and Otte. Termination of cyanoacrylate polymerization occurs under two conditions: 1) all of the available monomer is consumed or 2) the growth of polymer is interrupted by the presence of an acidic species.⁴⁶ Simulations of alkyl cyanoacrylate polymerizations similarly show continual steady propagation, independent of chain length, until terminated by a cation.⁴⁷

Many protocols for CFM suggest 80% relative humidity as the optimum humidity to obtain the most poly(ethyl cyanoacrylate) on print ridges. This is often ascribed to the fact that above 75% relative humidity, the NaCl in the fingerprint residue absorbs water, which increases the rate of initiation of the polymerization. Paine et al studied the effect of humidity on the quality of print and microstructure of the formed poly(ethyl cyanoacrylate) in groomed eccrine and sebaceous prints. For both types of prints, the hands were washed, rinsed with ethanol, and completely air dried. Donors for groomed eccrine prints wore latex gloves for 30 minutes before depositing prints while the donors for groomed sebaceous prints, rubbed their fingers along oily parts of their face (i.e. nose or forehead) immediately after drying and prints were subsequently deposited. For groomed eccrine prints, the average fingerprint grade increased steadily with relative humidity up to 85 percent while sebaceous prints showed no correlation between fingerprint grade and relative humidity. The PECA fumed from eccrine components were

noodle-like in structure while sebaceous prints produce PECA that is more like a flat, thin film containing nodular structures. Paine et al report when the print is fumed at relative humidities of 70 to 90%, there is an increase in the contrast between the ridge and background creating a higher quality print than when they are fumed at lower humidities. They also found that the eccrine components were more sensitive to variations in the levels of relative humidity with fingerprint grade increasing as relative humidity increases.⁴⁸ This is attributed to the eccrine prints being primarily composed of water and water-soluble components. The development of eccrine prints at lower humidity were faint, while at high humidity, large amounts of background development occurred, reducing the contrast. For the development of sebaceous fingermarks by the CFM, there was a slight increase in mark quality at 70 and 79% relative humidity but the relationship between print quality and humidity was not clearly demonstrated. This may be due to the mucoproteins in sebaceous deposits that can limit penetration of water into the print. This would result in little variation in print quality with change in humidity when fuming sebaceous prints.⁴⁸

Algaier et al. also investigated the impact of fuming temperature variation, from 20 – 80 °C, on the success of the fuming of latent prints. This study found that decreasing temperature increased the amount of poly(ethyl cyanoacrylate) grown on the surface of fingerprint ridges, with the largest amount of polymer obtained at 10-20 °C. Temperature did not have a significant role in the molecular weight of formed PECA.²² The fuming of the print with ECA at low temperatures and standard humidity produces a larger quantity of polymer on the print.^{17, 49} The ion pair is more loosely bound at lower temperatures. In addition to lower temperatures providing an environment in which there is an increase in

initiation, the rate of propagation is also increased for solvated ions leading to more dense polymer on the surface of the print.²²

Therefore, the current understanding is that higher humidity at normal fuming temperatures (30-50 °C) solvates the ion pair at the growing polymer chain end, benefiting the polymerization process and print quality. At the same time, lower fuming temperatures create a looser ion pair at the polymer chain end, also benefiting the polymerization process and print quality. However, at high humidity and lower temperatures, there exists the possibility that water will condense on the print and evidence, creating background polymer that decreases print quality. Therefore, there is a need to understand the *combined* effect of humidity and temperature on the ECA fuming process to provide a fundamental understanding of these competing processes and offer insight that will foster a more effective protocol for forensic scientists to retrieve latent prints from a crime scene.

Experimental

Print Deposition

In order to produce the most consistent print composition as possible, the following steps were taken to reproducibly deposit prints onto the surfaces: First, hands are washed with non-fragrant liquid soap for 10 minutes. The hands are then air-dried. Once the hands are dry, the finger is rubbed against an oily area of the face, such as forehead or nose. A print is then deposited by lightly rolling the finger across the surface.

Cyanoacrylate Fuming Method for Variable Surface Temperature and Relative Humidity

To aid in the understanding of the set-up of these experiments, the apparatus is shown and labeled in Figure 2-1. This is a single fuming protocol in which a hot plate (G) set to 150 °C is used to vaporize the ethyl cyanoacrylate monomer in an Aluminum dish (F) for a fuming time of 10 minutes. To control the surface temperature of the substrate (E), a copper block (C) attached to an Isotemp 3016 temperature controller (D) was placed on the back of the substrate which is attached to a ring stand. The surface temperatures were measured pre- and post-fuming with an infrared thermometer (H). The surface temperatures studied are as follows: -10, 0, 5, 10, 15, 20 and 25 °C. The fuming experiments were completed at ambient, 50%, and 80% relative humidity. For ambient studies, no additional humidity was introduced into the system via the humidifier (A). For 50 and 80%, the humidifier was turned on and additional humidity flowed into the system until the desired relative humidity was obtained. The relative humidity was monitored using a hygrometer (B) throughout the fuming process. The knobs on the humidifier were adjusted to maintain the desired setting for 50 and 80% relative humidity. For timed studies, this protocol was carried out for the following times: one, two, three, five, seven and a half, and ten minutes.

Gel Permeation Chromatography

The PECA that forms on the substrates with fumed prints was sonicated in tetrahydrofuran (THF) for ten minutes to dissolve the PECA. Subsequently, the samples were analyzed via gel permeation chromatography (GPC) utilizing a Tosoh Bioscience

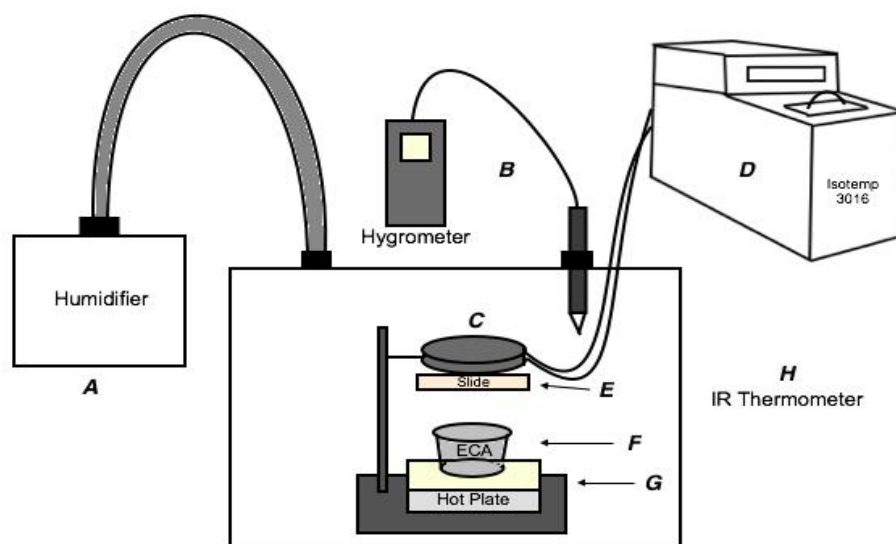


Figure 2-1: Labeled apparatus for the cyanoacrylate fuming method

EcoSEC instrument equipped with two cross-linked poly(styrene/divinylbenzene) columns. The flow rate was 0.35 mL/min at a temperature of 40 °C with a polystyrene calibration and a refractive index detector used during the analysis. The total retention time observed for all samples was 15 minutes.

Results and Discussion

Cyanoacrylate Fuming Method for Variable Surface Temperature and Relative Humidity

The cyanoacrylate fuming method was conducted over a range of surface temperatures and relative humidities on glass using Sirchie OMEGA Print as the cyanoacrylate formulation. Since high humidity and low temperature introduce the possibility of condensation into the system, this could influence the overall amount of poly (ethyl cyanoacrylate) on the slide. Figure 2-2 shows a visual comparison for the glass slides (in triplicate) that are fumed under different relative humidities over the surface temperature range. For the samples fumed at lower surface temperatures, below 10 °C, under ambient relative humidity, there is a large amount of background polymerization, with growth of polymer occurring on the substrate as opposed to solely on the fingerprint. We ascribe this result as due to the condensation which occurs when the substrate is cool and excess moisture accumulates on the surface. Excess moisture occurred on all of the substrates fumed under 50 and 80% relative humidity causing overdevelopment (polymerization on and between the ridges of the print) for all of those samples. For all humidities, the condensation decreased as the surface temperature increased.

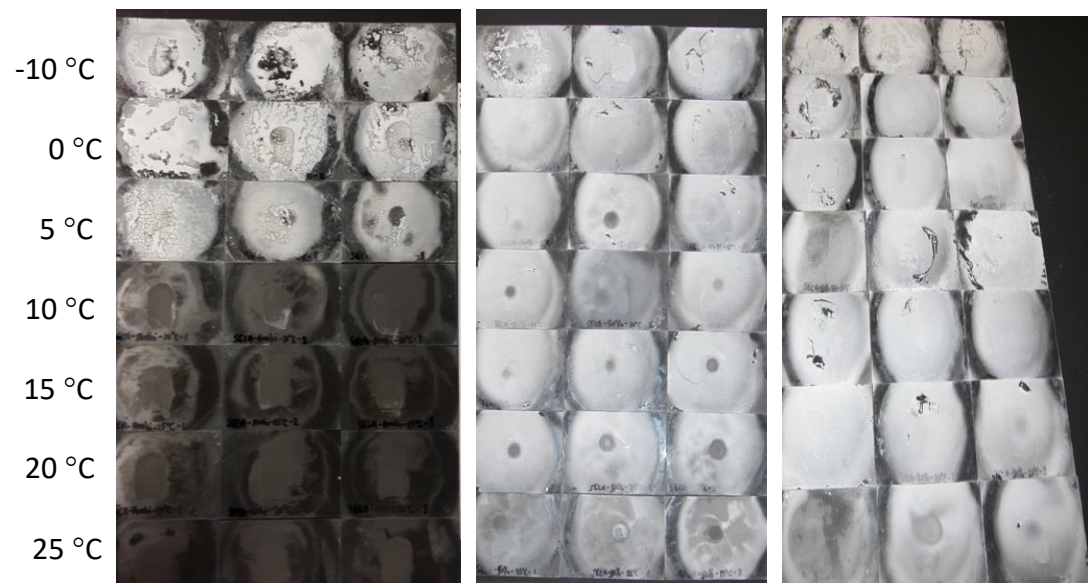


Figure 2-2: Photos of slides after fuming at surface temperatures from -10 to 25 °C at ambient (left), 50% (center) and 80% (right)

The effect of surface temperature and relative humidity on the amount of poly(ethyl cyanoacrylate) (PECA) formed during the fuming process is shown in Figure 2-3. The overall average mass of PECA increased as relative humidity increased. The increase in moisture solvates the ion pairs on the growing chain end resulting in faster initiation and propagation. Ambient relative humidity is the only condition in which the correlation of humidity and surface temperature change can be clearly observed. When fuming at ambient relative humidity, lowering the surface temperature produces more PECA. This change in amount of PECA formed with temperature is not as apparent as the relative humidity increases. Lowering the surface temperature at a relative humidity at 50% results in an increase in PECA grown with decreasing temperature at higher temperature, but the amount of PECA formed levels off below about 5 °C. Alternatively, at 80% relative humidity, the optimum mass of PECA formed occurs around 14 °C. Based on results reported by Paine et al, the quality of the print increases as the relative humidity increases. Those studies were done at room temperature without any surface temperature control. As a result, condensation was of little concern. The condensation of water on the surface is expected to inhibit chain growth polymerization, as it introduces protons which are known terminators for anionic polymerization. Another determining factor playing a vital role in the polymerization is the decrease in surface temperature. Lower temperatures inhibit side reactions, including termination and chain transfer reactions in anionic polymerizations. As a result, the molecular weight should increase as the temperature decreases. This effect competes, or conflicts, with those of the impact of relative humidity. In order to understand the molecular origin of this behavior and how the

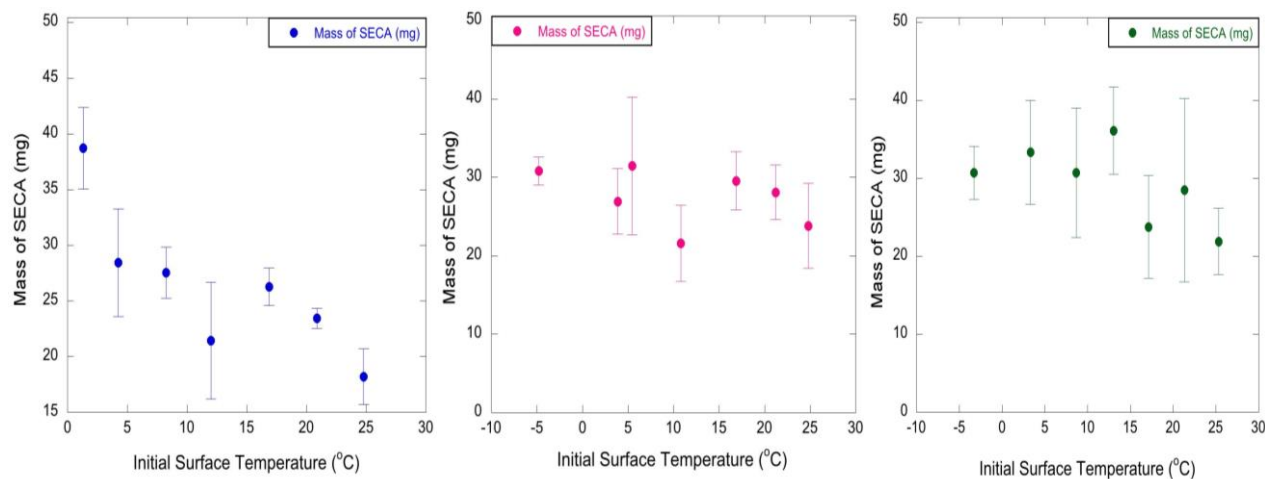


Figure 2-3: Average mass of poly (ethyl cyanoacrylate) on glass slides after fuming at surface temperatures ranging from -10 to 25 °C at ambient, 50%, and 80% relative humidity

polymerization affects the amount of PECA for all of the samples, the molecular weight of the formed PECA was investigated for each relative humidity and temperature setting.

Gel permeation chromatography was used to analyze the samples and obtain molecular weight characteristics of the samples. In order to analyze samples via GPC, the sonicated PECA:THF solutions were filtered. This filtration may result in the removal of crosslinked polymer. Figure 2-4 shows that increasing the relative humidity for the cyanoacrylate fuming produces lower molecular weight (M_w or M_n) of soluble polymer. Note: The scales for the vertical axes vary with relative humidity in Figure 2-4. These results indicate that despite higher relative humidity producing a larger quantity of PECA, as seen in Figure 2, the chains of the polymer are much shorter than those resulting from fuming at lower relative humidity. For anionic polymerizations, such as the polymerization of PECA, the higher moisture content in the system, can cause chain termination and lead to shorter chains and lower molecular weights of the polymer. The added moisture provides excess protons in the reaction, which are common terminating agents for anionic polymerization. Therefore, the larger amount of PECA formed at higher relative humidity is attributed to a larger amount of short chain polymer. Overall, ambient relative humidity provided the highest molecular weight polymer. As reported by Algaier et al, surface temperature does not greatly affect the molecular weight of PECA. Based on these results, the relative humidity has a more dominant effect on the polymerization than surface temperature when the CFM is performed on surfaces at and below room temperature.

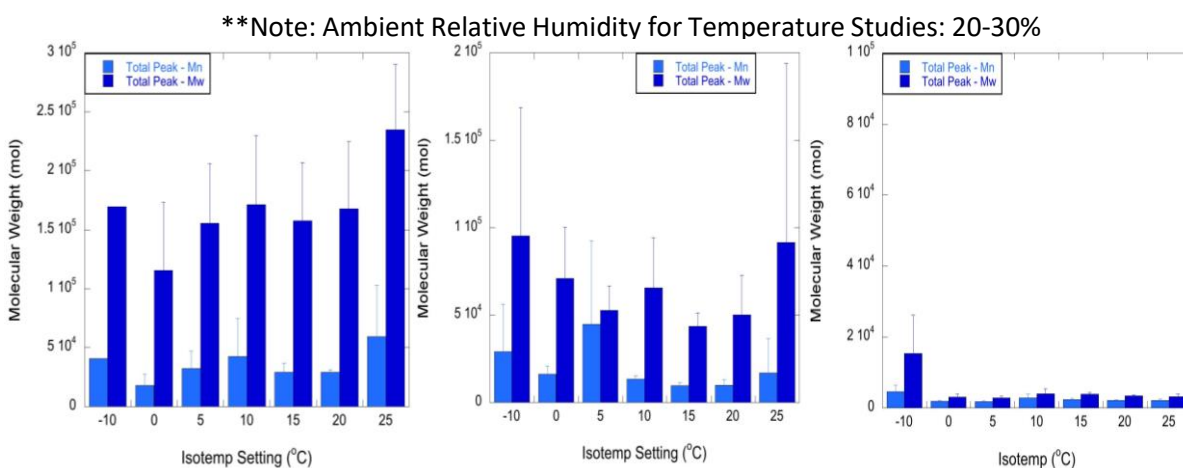


Figure 2-4: Molecular weight characteristics of poly (ethyl cyanoacrylate) for surface temperatures from -10 to 25 °C when fuming at ambient (left), 50% (middle), and 80% (right) relative humidity.

Time Evolution of Print Development

Based on Figure 2-2, the most detailed prints to the untrained eye were observed when the isotherm was set to 10 °C for all relative humidity studies. Because our primary goal is to determine the optimum parameters to achieve the best visual quality, we further investigated PECA polymerization at a surface temperature of 10 °C with our primary focus being the effect of fuming time on the amount of PECA and the characteristics of the resultant PECA polymer. When fumed at 50 and 80% relative humidity, all of the samples appeared to be overdeveloped. Figures 2-5 and 2-6 depict the change in the visual quality and mass of formed PECA, respectively, for the cyanoacrylate fuming method when carried out from one to seven and a half minutes.

Visually, Figure 2-5 depicts no occurrence of background polymerization for substrates fumed under ambient relative humidity for any fuming time. Very minimum background occurs at the shorter fuming times when fuming at 50% relative humidity. At 80% relative humidity, there is a substantial amount of background polymerization for every fuming time. For 50 and 80% relative humidity, there is an apparent increase in background polymerization as fuming time increases. At five and seven and a half minutes, the appearance of prints are greatly minimized by the background polymerization to the point in which the details of the print cannot be clearly seen in photographs.

Figure 2-6 shows that the average mass of PECA consistently increases over time for all relative humidities. Below three minutes, the amount of PECA on the surface is similar for all relative humidities. As time increases, higher relative humidities produce



Figure 2-5: Photos of slides after fuming at a surface temperature of 10 °C at ambient (left), 50% (middle) and 80% (right) relative humidity over time.

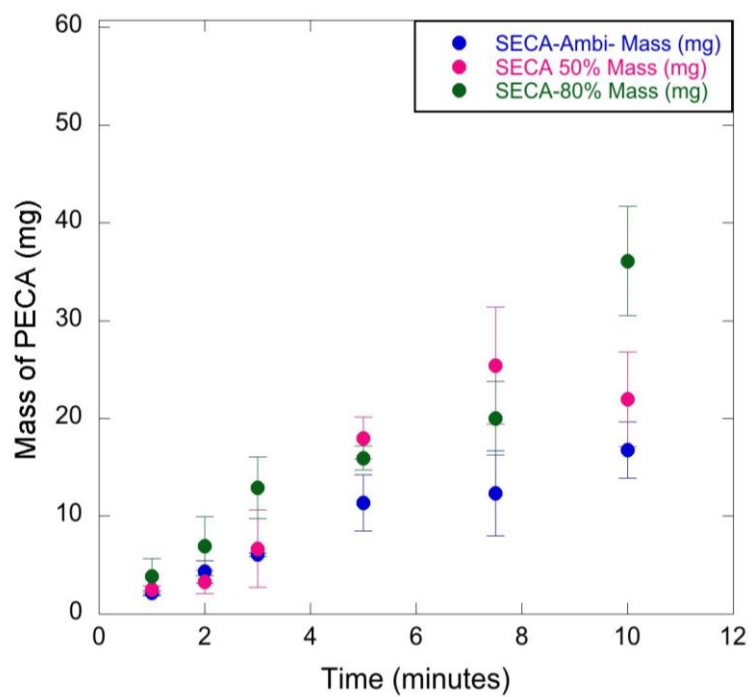


Figure 2-6: Average mass of poly (ethyl cyanoacrylate) on glass slides after fuming at a surface temperature of 10 °C at ambient, 50%, and 80% relative humidity.

larger amounts of PECA on the surface. At five minutes and greater, the clear advantage of the higher mass at higher humidity becomes less apparent as the averages (with standard deviations) of 50 and 80% relative humidities began to level off.

To determine if fuming time affects the molecular weight characteristics of the formed PECA, samples were analyzed via GPC. As was previously seen with the study of varying surface temperature, Figure 2-7 depicts higher relative humidity led to lower average molecular weights. The number and weight average molecular weights for each relative humidity as a function of fuming time mimicked trends observed with surface temperature variation. As relative humidity increased, the average molecular weights decreased.

For ambient humidity, the molecular weight of the formed polymer does not vary significantly with fuming time. For 50% relative humidity, there is a Mw increase from 1 to 2 minutes of fuming but a decrease in chain length as fuming time increased. We propose that this decrease in Mw as fuming time is due to the increased interaction of ECA vapors with moisture in the air of the tank which causes chain termination for anionic polymerization. The highest molecular weight polymer is obtained at two minutes for 50% relative humidity but the maximum amount of PECA on the surface occurs at eight minutes. At five minutes, the average mass of PECA formed for 50% relative humidity is comparable to the average mass of PECA formed for ambient relative humidity at 10 minutes. At about four minutes, the benefits of a slightly decreased surface temperature and shorter fuming time may be the key parameters for fuming at 50% relative humidity. The high moisture content appears to control the molecular weight characteristics for

****Note: Ambient Relative Humidity for Time Evolution: $\leq 10\%$**

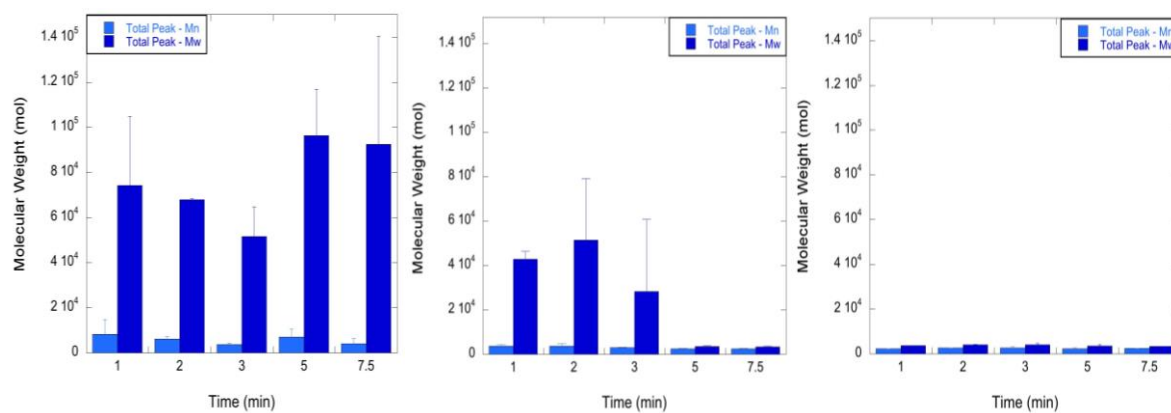


Figure 2-7: Molecular weight characteristics of poly (ethyl cyanoacrylate) as a function of fuming time for surface temperature of 10 °C when fuming at ambient (left), 50% (middle), and 80% (right) relative humidity.

PECA fumed at 80% relative humidity in which all Mn and Mw values were relatively low with no significant change in polymer molecular weight over the fuming times.

Conclusion

This data serves to elucidate the importance of surface temperature and humidity on the cyanoacrylate fuming method, which should be beneficial to the forensic community. Of the relative humidity settings tested, the cyanoacrylate fuming method carried out under ambient relative humidity produces more high molecular weight poly(ethyl cyanoacrylate) and the optimum contrast for the effective retrieval of detailed latent fingerprints. The prints developed under higher relative humidities are often overdeveloped due to the high content of water in the fuming chamber. These higher relative humidities also correlate with large amounts of PECA on the surface and large amounts of low molecular weight polymer.

When expanding the study to investigate how fuming time affects the PECA formed in the cyanoacrylate fuming method under different relative humidities, lower humidity was found to be less likely to overdevelop and produced longer polymer chains. The longer fuming times led to larger amounts of PECA formed but also produced a large amount of short chains when the relative humidity was 50 or 80 percent. The larger amounts of PECA is ascribed to the presence of water, loosening the ion pairs of the cyanoacrylate at the growing end of the polymer chain. The lowering of surface temperature also minimizes side reactions that may be responsible for destroying propagating chain ends. The presence of protons in condensed water can also serve to

terminate chain propagation. The coupling of the lowered surface temperatures and high humidity gives rise to condensation on the surface, which increases the probability of termination, particularly at higher relative humidity. Overall, these results show controlling the surface temperature of the substrate in addition to the relative humidity can be very beneficial in attaining the optimum quality and contrast of the print.

**CHAPTER 3 : INVESTIGATING THE EFFECT OF CYANOACRYLATE
FORMULATIONS ON THE EFFICIENCY OF THE CYANOACRYLATE
FUMING METHOD**

Abstract

Cyanoacrylate is an adhesive commonly known as superglue. Cyanoacrylate is used in the cyanoacrylate fuming method (CFM) in the forensics field to visualize latent prints at a crime scene. The fuming proceeds via the reaction of ethyl cyanoacrylate (ECA) with biological components that exist in fingerprints, which initiates the anionic polymerization of ECA. The formulation of ECA used in the CFM has been modified to enhance the fuming process and improve the production of poly(ethyl cyanoacrylate) (PECA) on the print. A popular modified ECA formulation is Lumicyano which contains a fluorescent compound, 3-chloro-6-ethoxy-1,2,4,5-tetrazine, which fumes with ECA to provide greater contrast in the developed print. This study examines the impact of the presence of the fluorescent tetrazine in the cyanoacrylate formulation on the polymerization of ECA during the fuming of latent prints. This is accomplished by monitoring the PECA produced by fuming Lumicyano relative to that formed when fuming Sirchie OMEGA-Print, which is a widely used ECA formulation in CFM. Our findings indicate Lumicyano is an advantageous formulation which produces a comparable amount of PECA relative to the unmodified ECA. However, the polymerization of the ECA when fuming Lumicyano is less prone to side reactions and chain termination than the polymerization of OMEGA-Print. We ascribe this to a coupling of the tetrazine with the ion pair at the growing chain end. We believe that this results in the tetrazine acting as a “protecting group” that limits side reactions and slows propagation. Lumicyano also has the added benefit of increased visualization due to enhanced contrast, especially when observed under ultraviolet light.

Introduction

There are a variety of components found in a human fingerprint, including eccrine sweat, sebum secretions, and water. Eccrine sweat, always present in fingerprints, is composed of a mixture of inorganic compounds (such as NaCl) and water-soluble organic compounds (such as urea and amino acids). Sebum secretions originate from oily areas of the body, such as the surfaces of the face and head, and include fat-soluble compounds such as glycerides, fatty acids, squalene (a precursor to steroids), sterols, etc.⁵

The cyanoacrylate fuming method (CFM) is used by forensic scientists to visualize latent prints on nonporous and semi-porous evidence found at crime scenes. In this method, the monomer, ethyl cyanoacrylate, is heated so that its vapors interact with the biological constituents found in prints. As these vapors interact with the amino acids, etc., the ECA polymerizes to form chains of poly(ethyl cyanoacrylate) (PECA) on the surface of the print, providing visual contrast between the print and its surrounding, making the print ridges more visible.

The Chemistry of the Cyanoacrylate Fuming Method

The chemical reaction that occurs during the fuming is an anionic polymerization, which is driven by the electron withdrawing character of the nitrile and ester groups of the cyanoacrylate. Figure 3-1 is a schematic of the anionic polymerization which governs the fuming process. In the presence of a nucleophile, the nitrile and ester groups become slightly negative, polarizing the double bond of the ethyl cyanoacrylate making the

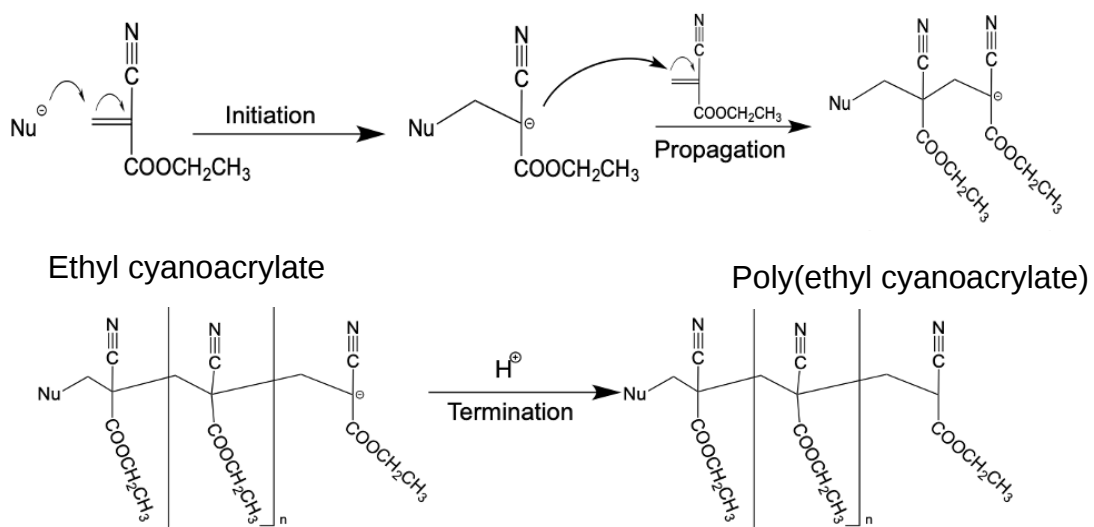


Figure 3-1: General mechanism for the anionic polymerization of ethyl-cyanoacrylate polymerization

monomer more susceptible to nucleophilic attack.⁵⁰ Propagation occurs when the electron deficient monomer inserts into the ion pair at the anionic chain end. Meanwhile, the cyano group and ester group substituents resonantly stabilize the negative charge of the growing chain end, as shown in Figure 3-2.^{14, 51} Wargacki et al tested the ability of sodium lactate and alanine as model components of eccrine sweat and water at different pH values to initiate the polymerization of ECA during the fuming process. The amount and chain length of polymer formed during fuming from water was significantly less than that of the polymer formed from alanine or sodium lactate solutions. This clearly shows that water is not the primary initiator of the ECA during fuming, though does initiate smaller polymer chains. This is one of the studies which found the carboxylate groups of the eccrine sweat components are primarily responsible for the initiation of the polymerization. Moreover, further studies show that higher pH leads to more polymer growth due to the reduction of terminating agents in anionic polymerization such as protons.¹⁶

Although previous studies have shown that water is not the primary initiator in the polymerization, it is found that the cyanoacrylate fuming process is more effective in higher humidity environments, and thus the humidity is a vital component in the cyanoacrylate fuming process. Wargacki et al found that the absence of water creates a local chemical environment that is less suitable for the growth of poly(ethyl cyanoacrylate) from the print bound initiators.⁴⁵ Their interpretation is that the water in humid air solvates the ion pairs at the growing chain end of the anionic polymerization of ethyl cyanoacrylate, which increases the rate of propagation. Similarly, Algaier et al. tested the effect of

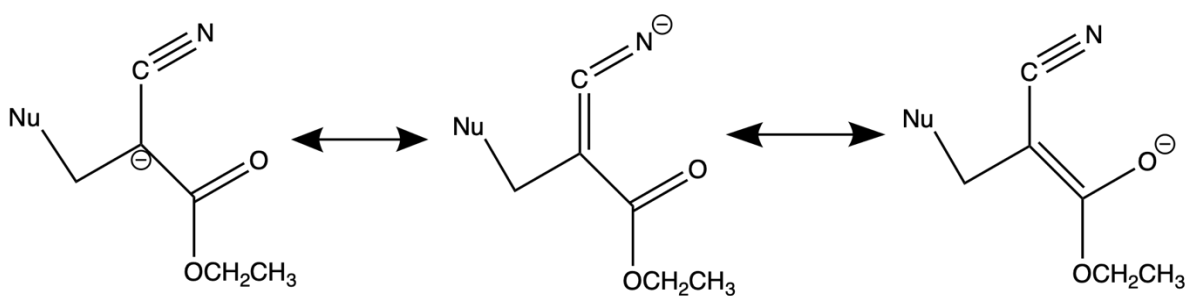


Figure 3-2: Resonance Stabilization of the α -carbanion of ethyl cyanoacrylate by cyano and ester substituents in the presence of a nucleophile.

counter-ion size using sodium, potassium and tetrabutyl ammonium (TBA) lactate solutions as initiator. As this is an anionic polymerization, the counter-ion is the cation paired with the anion that initiates the polymerization and resides at the anionic growing chain end. They found TBA, which is the largest counter-ion, produced the most polymer. As the larger counter-ion forms a more loosely bound ion pair, these results emphasize the importance of the nature of the ion pair in the polymerization. These results were compared to the impact of changing temperature on the polymerization of ECA during fuming, which led to the conclusion that creating an reactive chain end with a loosely bound ion pair leads to an improved polymerization of ECA in the CFM process.²²

Many protocols for CFM suggest 80% relative humidity as the optimum humidity to obtain the most poly(ethyl cyanoacrylate) on print ridges. Paine et al. report that when a print is exposed to relative humidities of 70 to 90% during fuming, there is an increase in the contrast between the ridge and background creating a higher quality print than prints that are fumed at lower humidities. In this study, three types of fingerprints were tested: "Natural", where hands were unwashed for 30 minutes before print deposition, "Groomed eccrine", where hands were washed then rinsed with ethanol followed by 30 minutes in latex gloves before print deposition, and "groomed sebaceous" where hands were washed, rinsed with ethanol and allowed to completely dry before rubbing the fingers on an oily area of the face before print deposition. All prints were deposited on brass and aged for one week before cyanoacrylate fuming took place. When exposed to increased relative humidity (60-100%), the eccrine prints showed the most detail, which was used to quantify the quality of the print.⁴⁸

Algaier et al. investigated how temperature variation, from 20 – 80 °C, affects the quality of the resultant polymer that is formed when fuming latent prints. They found that decreasing temperature resulted in a swifter development of ECA with an increased amount of poly(ethyl cyanoacrylate) grown on the surface of fingerprint ridges, with the largest amount of polymer obtained at 20 °C. The temperature of fuming did not significantly alter the molecular weight of PECA formed by fuming.²² The polymerization of ECA at low temperatures and ambient humidity produces a larger quantity of polymer in the fuming process.^{17, 49} Temperature also affects the morphology, or micron level shape, of the fumed poly(ethyl cyanoacrylate). Smooth, globular PECA is typical of higher fuming temperatures and a more open fibrillar steel wool morphology is common at lower temperatures.⁴⁹ Based on these studies, higher moisture and low temperature appear to be preferred conditions for fuming.

One risk of lower temperature at higher relative humidity is condensation of water on the surface, which can serve as a source of background PECA formation and decrease the quality of the print. In well-controlled anionic polymerizations, water is usually completely removed from the system because it can act as a terminator to the propagation of the monomer. In Chapter 2, we studied the combined effects of relative humidity and surface temperature to understand their collective impact on the fuming process. These results showed that higher relative humidity produced lower molecular weight polymer and overdeveloped the print, to the extent that the print was not detectable. In contrast, ambient relative humidity paired with lower surface temperatures led to a significant

growth of poly(ethyl cyanoacrylate) as well as high molecular weight polymer from the cyanoacrylate fuming method while maintaining high quality, visually discernible, prints.

In order to gain insight into the important chemical processes in the cyanoacrylate fuming method, Wargacki et al studied the impact of different variables on the morphology, mass, and molecular weight of PECA formed with cyanoacrylate fuming. One factor examined was pH in which they studied the growth of PECA by fuming under acidic, neutral, and basic conditions for three minutes. They found an acidic environment resulted in little to no change in mass of PECA when compared to neutral pH and there was limited chain growth producing modest molecular weight oligomers, resembling the products of fuming pure water.^{16, 52} Conversely, fuming with higher pH increased the mass and molecular weight of the formed PECA, when compared to neutral and acidic conditions. Fuming under basic conditions produced long chain polymers which enhanced visual contrast of the fingerprint on the surface. The variation in mass and molecular weight of the PECA with pH were only significant after fuming for one minute. This indicates that pH influences the latter parts of the polymerization rather than the initiation. This was interpreted to indicate that the acidic environment suppresses propagation and enhances termination, leading to an increase in the number of PECA chains formed.^{16, 52}

Enhancing Print Visualization

Often, cyanoacrylate fuming is followed by a post-treatment, such as the deposition of a dye reagent on the print, which further enhances the contrast and visibility of the fumed prints without compromising DNA evidence that may be present. To minimize the amount of time for CFM, modified ECAs have been formulated and commercialized as an alternative to fuming with neat ECA. Lumicyano, a mixture of ethyl cyanoacrylate and a tetrazine based fluorophore, offers a one-step ethyl cyanoacrylate fuming process. This formulation is popular in Europe, where Figure 3-3 shows the chemical structure of the ECA monomer and the tetrazine based fluorophore (3-chloro-6-ethoxy- tetrazine) in Lumicyano. Tetrazine is an aromatic six membered ring with four nitrogen atoms. The presence of the nitrogen atoms in the aromatic ring causes an inductive effect due to the higher electronegativity of the nitrogen atoms.⁵³ 1,2,4,5 tetrazines, or s-tetrazines, are electron poor, consisting of a strong electron deficient tetrazine core and is a strong electron acceptor.³² Based on this, the incorporation of the fluorescent tetrazine, 3-chloro-6-ethoxy-1,2,4,5 tetrazine, may alter the reactivity of the polymerization process.

In contrast to mixing ECA with a fluorophore, Groeneveld et al bonded a fluorophore to the cyanoacrylate monomer to formulate a fluorescent cyanoacrylate that will stain ECA deposits, enhance the visibility of prints and reveal previously unseen prints without degrading biological evidence with the copious use of solvents.³⁷ They referred to their formulation as “Oligocyano”. Additionally, they used size exclusion chromatography (SEC) to compare the average molecular weights of PECA that is formed

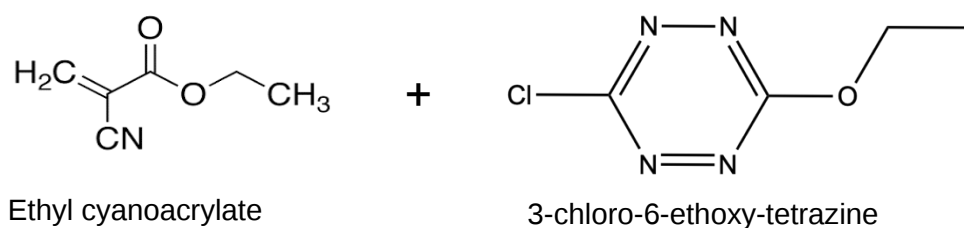


Figure 3-3: Lumicyano formula: Ethyl cyanoacrylate with the fluorophore additive

By fuming prints with fluorescent cyanoacrylates already on the market (CN-Yellow, Lumicyano and Polycyano UV) and with their Oligocyano ECA formed in lab. Of the formulations tested, Lumicyano formed the largest molecular weight polymer by fuming of the commercially available products and their Oligocyano formulation.³⁷

The morphology of PECA on the fumed fingerprints developed with Lumicyano consist of slightly more highly developed dendritic nanofiber morphology in comparison to the morphology of PECA formed from regular cyanoacrylate fuming. The morphology of the PECA obtained by fuming with Lumicyano is attributed to the addition of the fluorophore in Lumicyano.³⁷ It is interesting that such a nanofiber morphology is more common when CFM is conducted in a basic environment,^{16, 52} suggesting that the tetrazine is more basic than acidic. If the tetrazine is indeed basic, the fluorophore will favor propagation, leading to the formation of longer PECA chains.³⁷ Prete et al. also reported that Lumicyano offers equal or better sensitivity for the detection of fingerprints when compared to prints that are fumed with traditional cyanoacrylate processes.⁵⁴

Farrugia et al investigated the efficiency of various fingerprint development processes, including dusting with iron-oxide powder suspension, cyanoacrylate fuming followed by treatment with the fluorescent dye, basic yellow 40 (BY40), and fuming with Lumicyano. All three methods produced viable prints, but Lumicyano is the only one step process with no additional wait time before analysis, making it more appealing as a visualization tool for forensic scientists.⁵⁵ These studies show that all of the enhancement techniques provide third-level ridge details and no overdevelopment. Of the visualization technique studied, Lumicyano detected about 16% more prints than the others, which is

speculated by the authors to be the result of Lumicyano's cyanoacrylate formulation when compared to conventional cyanoacrylate products.⁵⁶ The specific component responsible for the difference in behavior was not specifically postulated by the authors, however.

Finally, Farrugia et al studied the double fuming of latent prints with Lumicyano and compared the quality of the developed print to those that are developed by conventional cyanoacrylate fuming. In this study, double fuming is defined as allowing a minimum of six hours to pass after initial fuming of a print before performing the CFM a second time on a previously fumed print. These studies determined that the additional fuming cycles were advantageous in the visualization of prints. Prints that were fumed with Lumicyano were much more likely to be detected after the second fuming, with 50 more prints detectable under visible light and roughly 100 more prints detected under fluorescence. It was postulated that the tendency for Lumicyano vapors to target ECA deposits to reinitiate polymer growth allows the first fuming to serve as initiation sites for new PECA growth that only become detectable after the second fuming. The second fuming also showed no indication of overdevelopment and the amount of Lumicyano used in the fuming has no significant effect on the number of detectable prints. Double fuming with conventional cyanoacrylate formulations showed very few additional prints detected. Also, double fuming did not overdevelop prints using conventional cyanoacrylate.⁵⁷

Ideally, anionic polymerizations are carried out under nitrogen to eliminate the presence of contaminants, i.e., water, oxygen, or proton donors, which inhibit the initiation of anionic polymerization, allow side reactions to occur, or cause chain transfer or termination. As discussed in previous chapters, the cyanoacrylate fuming method is not

a well-controlled anionic polymerization with an environment completely devoid of contaminants. The addition of fluorescent dyes, as is the case with ECA formulations such as Lumicyano, aid in the visualization of fingerprints in evidence processing but this alteration of ECA formulation introduces another component which could inhibit the anionic polymerization during fuming. Lumicyano will be examined to assess the role of the additional fluorescent dye on the progress of the anionic polymerization of ECA. Fingerprints deposited on glass slides will undergo the cyanoacrylate fuming method with varying surface temperature and ambient relative humidity using the Lumicyano formulation of ECA as well as the Sirchie OMEGA-Print formulation, which we will denote as an unmodified formulation. Understanding the impact of the change in cyanoacrylate formulation on the polymerization of ECA during the fuming process provides insight that can be used by forensic scientists to optimize the cyanoacrylate fuming method and improve the visualization of fingerprints when utilizing fluorescent ECA formulations.

Experimental Details

Print Deposition

This work utilized multiple prints from a single donor. In order to produce the most consistent print composition as possible, the following steps were taken to deposit prints onto the surfaces: First, hands are washed with non-fragrant soap for 5 minutes. The hands are then air-dried. Once the hands are dry, the finger is rubbed against an oily area

of the face, such as forehead or nose. A print is then deposited by lightly rolling the finger across the surface.

Cyanoacrylate Fuming Methods

There were two different protocols utilized for cyanoacrylate fuming in our studies. To aid in the understanding of the set-up of these experiments, the apparatus is shown and labeled in Figure 3-4. The Sirchie OMEGA-Print protocol is the standard method to fume cyanoacrylates in our lab. For this protocol (CFM-S-HP150 °C-10 m), a hot plate (A) is set to 150 °C and vaporizes the ethyl cyanoacrylate monomer that is in an Aluminum dish (B) for a fuming time of 10 minutes. To control the surface temperature of the substrate (C), a copper block (D) attached to an Isotemp 3016 temperature controller (E) was placed on the back of the substrate which rests on an O-ring attached to a ring stand. The surface temperatures were measured pre- and post-fuming with an infrared thermometer (F). The surface temperatures studied include -10, 0, 5, 10, 15, 20, 25, 35 and 50 °C. The base fuming time was 10 minutes for most runs (CFM-S-HP150 °C-10 m), but some studies examined fuming time as a variable and thus fuming was completed for 1, 2, 3, 5, 7.5 and 20 minutes (CFM-S-HP150 °C-20 m) as well.

A second fuming method is exclusively used for Lumicyano and is based on the manufacturer's recommended protocol for Lumicyano (CFM-L-HP120 °C-20 m). The Lumicyano kit consists of the "Lumicyano powder" and the "Lumicyano solution", which is the ECA monomer. Crime Scene Technology, the manufacturers of Lumicyano, use the term "Lumicyano solution" to refer to their liquid ECA monomer, however the ECA is not

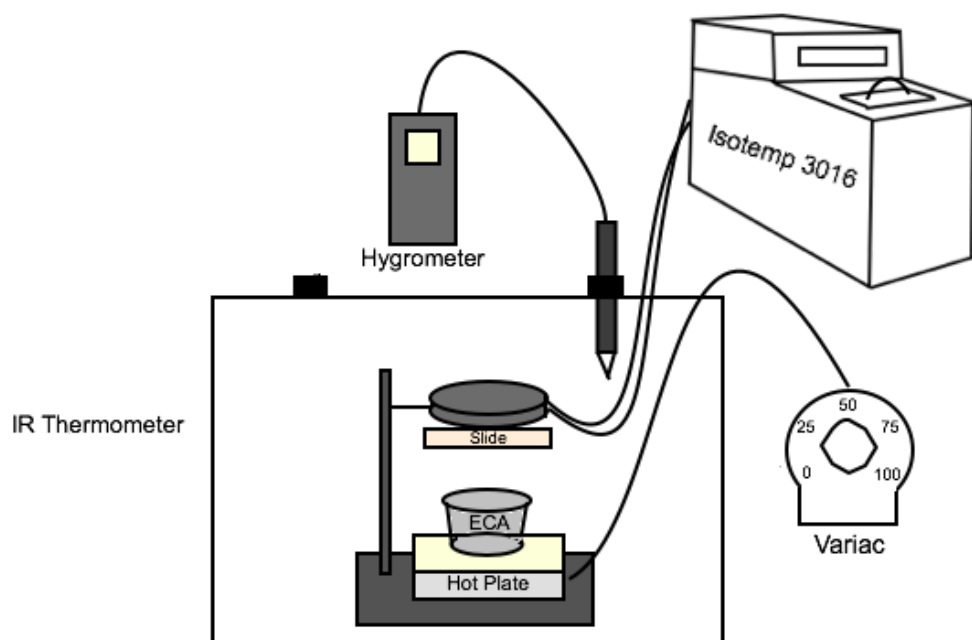


Figure 3-4: Labeled apparatus for the cyanoacrylate fuming method (CFM).

dissolved in a solvent. The Lumicyano powder is dissolved in the “Lumicyano solution” to give a final concentration of 5% Lumicyano powder to 95% Lumicyano solution. For clarity, “Lumicyano” will be the term used to represent the final mixture of the Lumicyano powder and “Lumicyano solution”. In this fuming protocol, CFM-L-HP120 °C-20 m, the 5% Lumicyano is slowly heated in the aluminum dish on a hot plate to 120 °C over 10 minutes and maintained at 120 °C for another 10 minutes, for a total fuming time of 20 minutes. A variac (G) controls the power output of the hot plate to maintain the temperature of the hot plate during fuming and ensure the desired hot plate temperature was not exceeded. Lumicyano was also fumed using the standard method for OMEGA-print described above, (CFM-L-HP150 °C-10 m), where a hot plate set to 150 °C vaporizes the ethyl cyanoacrylate monomer that is in an Aluminum dish for a fuming time of 10 minutes.

Gel Permeation Chromatography

The fumed prints on the substrate were diluted in tetrahydrofuran (THF) and sonicated for ten minutes. Subsequently, the PECA samples that dissolved in the THF were analyzed via gel permeation chromatography utilizing a Tosoh Bioscience EcoSEC instrument equipped with 2 cross-linked poly(styrene/divinylbenzene) columns. The flow rate was 0.35 ml/min at a temperature of 40 °C with a polystyrene calibration and a refractive index detector used during the analysis. The total retention time observed for all samples was 15 minutes.

Results and Discussion

The fluorescent cyanoacrylate, Lumicyano, was fumed utilizing two different protocols, the first being the Lumicyano recommended procedure (CFM-L-HP120 °C-20 m), and the other uses our standard fuming protocol (CFM-L-HP150°C-10 m). Based on our previous studies described in Chapter 2, all of the fuming protocols were carried out under ambient relative humidity.

Impact of Cyanoacrylate Formulation on Surface Temperature Dependence of Fuming

To identify how the fuming protocol and cyanoacrylate formulation impact the efficiency of the fuming of latent prints, prints were fumed with Lumicyano under the manufacturer's protocol, CFM-L-HP120 °C-20 m, and compared to prints that are fumed with Sirchie using our standard lab protocol CFM-S-HP150 °C-10 m. Figure 3-5 shows the visual appearance of fingerprints fumed on glass utilizing Lumicyano and its manufacturer's suggested protocol. Overdevelopment is evident for the prints fumed below 5 °C as the fingerprint is indiscernible due to excessive background polymerization. In other words, polymerization has occurred on the fingerprint as well as in between the ridges of the fingerprints and on the substrate of the deposited print. When humidity is combined with low temperature, condensation occurs. Though water is not the primary initiator in the fuming of latent prints, it can serve as a weak initiator for the polymerization of ethyl cyanoacrylate. Thus, the condensation leads to the polymerization of ECA on the

surface in addition to the polymerization occurring on fingerprints, causing background polymerization and overdevelopment.

Figure 3-6 shows the average mass of PECA on the glass slides after fuming Lumicyano with the CFM-L-HP120 °C-20 m protocol. Fuming at surface temperatures below 10 °C form over 40 mg of PECA on the glass slide. In the results presented in chapter two, as well as the visual analysis of the glass slides in Figure 3-5, we see an increase in mass of PECA at lower surface temperatures correlating with a higher occurrence of condensation. Figure 3-7a shows the molecular weight of the PECA formed from this fuming process and indicates that there is a significant increase in molecular weight of the PECA formed when fumed near the surface temperature of 10 °C. The decrease in molecular weight as the surface temperature increases mimics the trend observed for the mass of PECA on the surface, supporting a decrease in initiation and propagation as well as an increase in side reactions with increased temperature. The decrease in PECA molecular weight for surface temperatures lower than 10 °C is ascribed to condensation on the surface, which promotes chain transfer and/or termination of the anionic polymerization.

The average number of chains (N_{ch}) in the PECA formed is calculated from the data using the following equation:

$$\text{Equation 1:} \quad N_{ch} = \frac{mass \times N_A}{M_n},$$

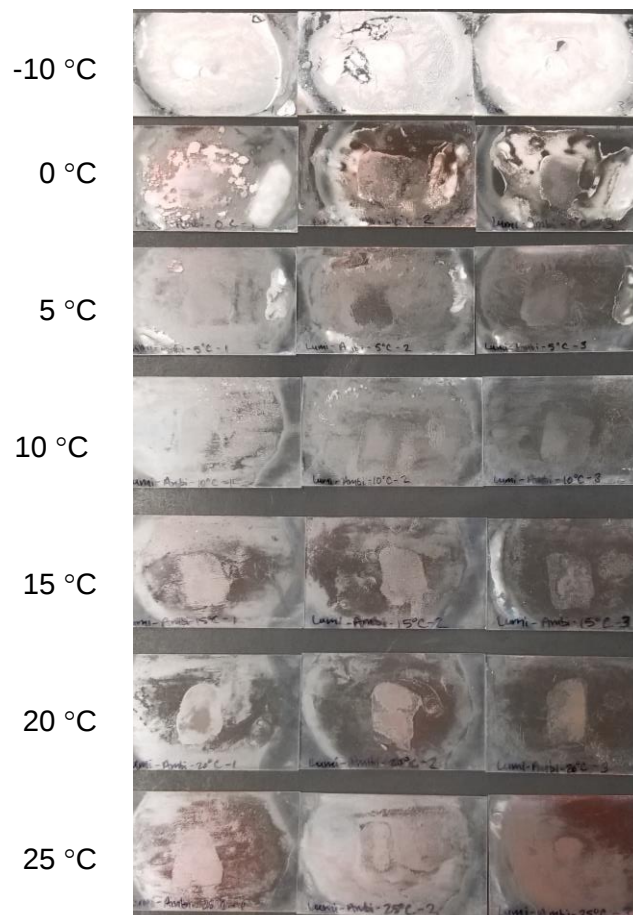


Figure 3-5: Visual appearance of poly(ethyl cyanoacrylate) on fingerprints for surface temperatures from -10 to 25 °C when fuming Lumicyano with protocol CFM-HP120 oC-20 m.

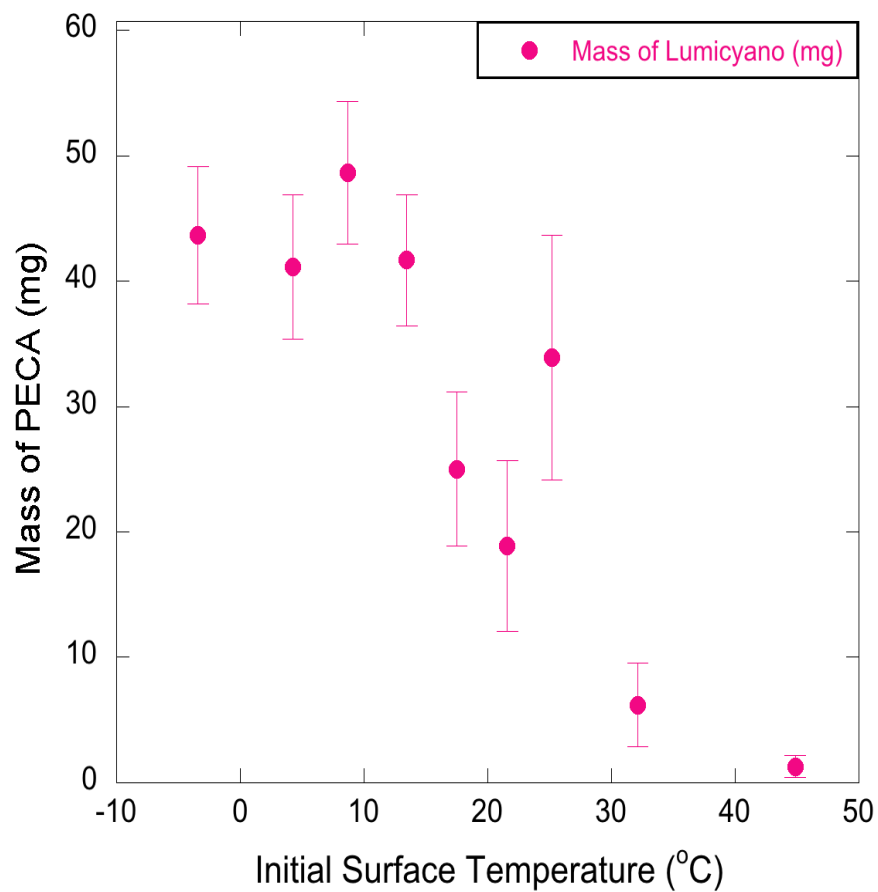


Figure 3-6: Average mass of poly(ethyl cyanoacrylate) on glass slides for surface temperatures from -10 to 50 °C when fuming Lumicyano with protocol CFM-HP120 oC-20 m.

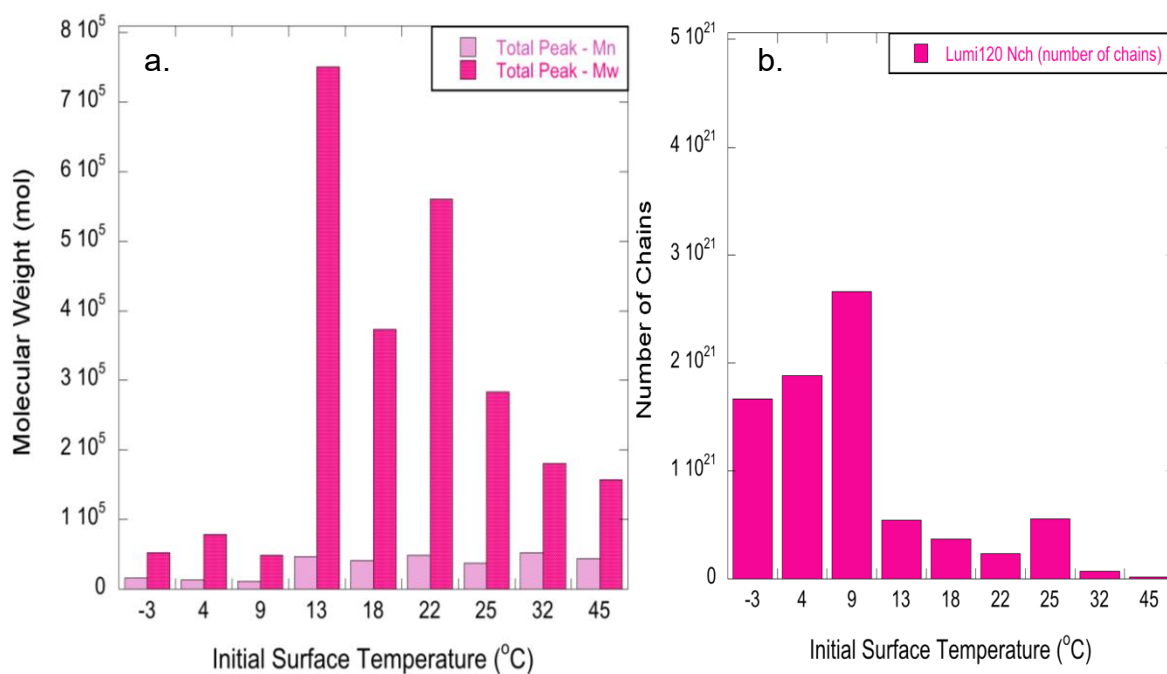


Figure 3-7: The (a) molecular weight of poly(ethyl cyanoacrylate) and (b) average number of chains for surface temperatures from -10 to 50 °C when fuming Lumicyano with CFM-L-HP120 oC-20 m protocol.

where mass is the average mass of PECA formed, N_A is Avogadro's number (6.02211×10^{23} molecules) and M_n is the number average molecular weight (g/mol) of the PECA formed. M_n is obtained from the GPC data. The average number of chains produced when the prints are fumed with Lumicyano at different surface temperature using the CFM-L-HP120 °C-20 m protocol are presented in Figure 3-7b. The decrease in the average number of chains as surface temperature increases is consistent with the interpretation that more termination and side reactions occur in anionic polymerizations at higher temperatures.

To provide insight into the role of ECA formulation on the fuming process, the Sirchie OMEGA-Print formulation of ECA was fumed for ten minutes with the hot plate set to 150 °C with surface temperatures of the print substrate ranging from about -10 to 50 °C. The average mass of PECA formed on the prints in these fuming processes are presented in Figure 3-8. This data shows the average mass of PECA formed when fuming the Sirchie cyanoacrylate using the standard protocol CFM- S-HP150 °C-10 m was lower than the average mass of PECA formed when the CFM was conducted with Lumicyano under the manufacturer's protocol, CFM-HP120 °C-20 m. The trend of decreasing amount of polymer formed on the print as surface temperature increases holds for both formulations.

Figure 3-9a presents the weight average molecular weight of PECA formed at different surface temperatures for polymer formed on prints that are fumed with Sirchie using the CFM-S-HP150 °C-10 m protocol. For Sirchie, the molecular weight fluctuates

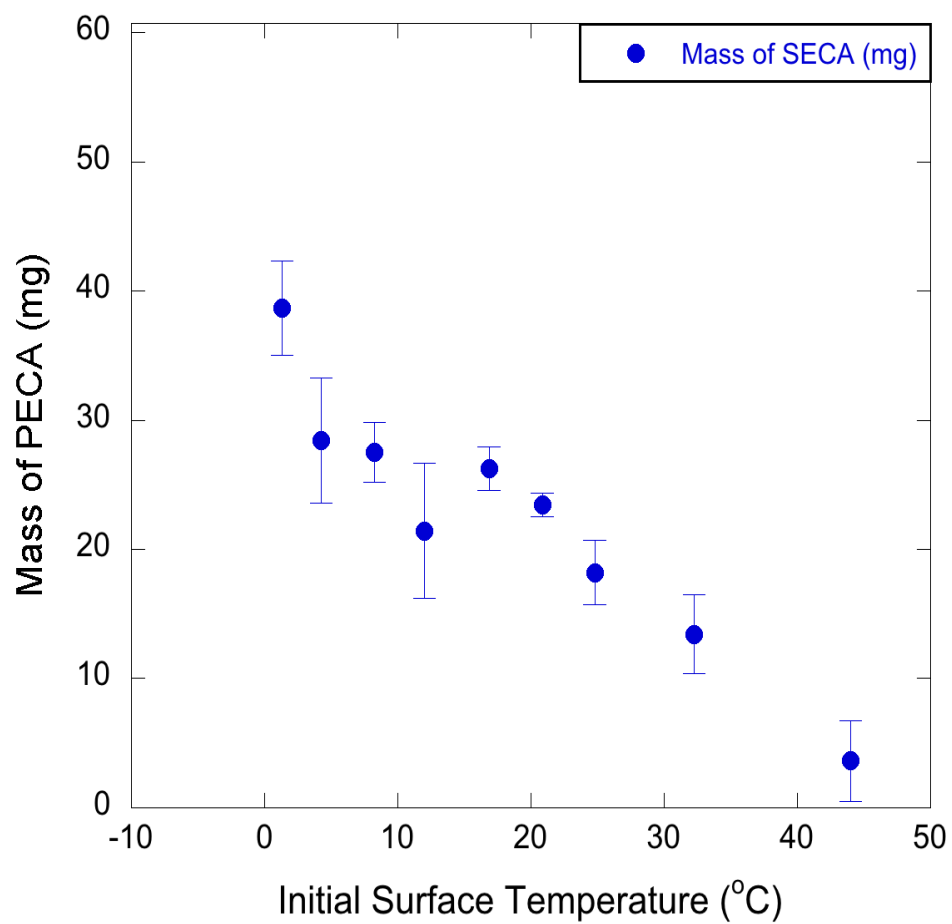


Figure 3-8: Average mass of poly (ethyl cyanoacrylate) on glass slides for surface temperatures from -10 to 50 °C when fuming Sirchie OMEGA-Print using fuming protocol CFM-S-HP150 oC-10 m.

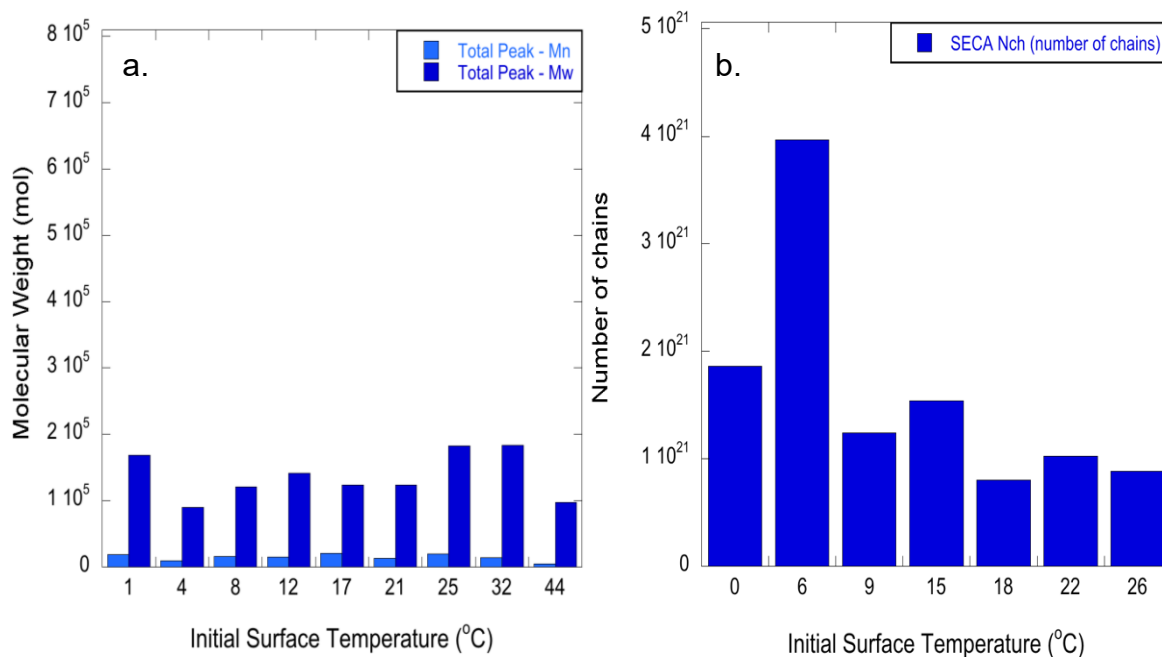


Figure 3-9: The a) molecular weight characteristics of poly(ethyl cyanoacrylate) and b) average number of chains for surface temperatures from -10 to 50 °C when fuming Sirchie OMEGA-Print with the protocol CFM-HP150 oC-10 m.

between the different surface temperatures and peaks at a much lower molecular weight than Lumicyano. Likewise, Figure 3-9b shows that the average number of chains that are formed during fuming is lower for the Sirchie formulation and protocol than for Lumicyano. This could be due to the slight variation in relative humidity between fuming, but may also be the result of the additional fuming time of the Lumicyano protocol. It is interesting that both formulations, although following different protocols (CFM-L- HP120 °C-20 m and CFM-S-HP150 °C-10 m protocols), have the largest number of chains at the lower surface temperatures. It may be that the increase in the average number of chains at lower surface temperature combined with the lower molecular weight PECA is due to the presence of contamination, such as water from condensation, which promotes chain termination throughout the fuming process. It is clear neither formulation benefits from fuming at surface temperatures above room temperature as there is very little PECA formed on the surface of the fingerprints at these temperatures.

Impact of Formulation on PECA obtained with the CFM-S-HP150 °C-10 m protocol

In order to understand the behavior of both formulations when fuming under identical protocols, Lumicyano and Sirchie were both fumed for ten minutes with the hot plate temperature set to 150 °C onto prints with controlled surface temperature from about -10 to 25 °C for a total fuming time of 10 minutes. As shown in Figure 3-10, the visual appearance of both formulations is similar for lower surface temperatures in that at temperatures below 10 °C, all developed prints have a large amount of background

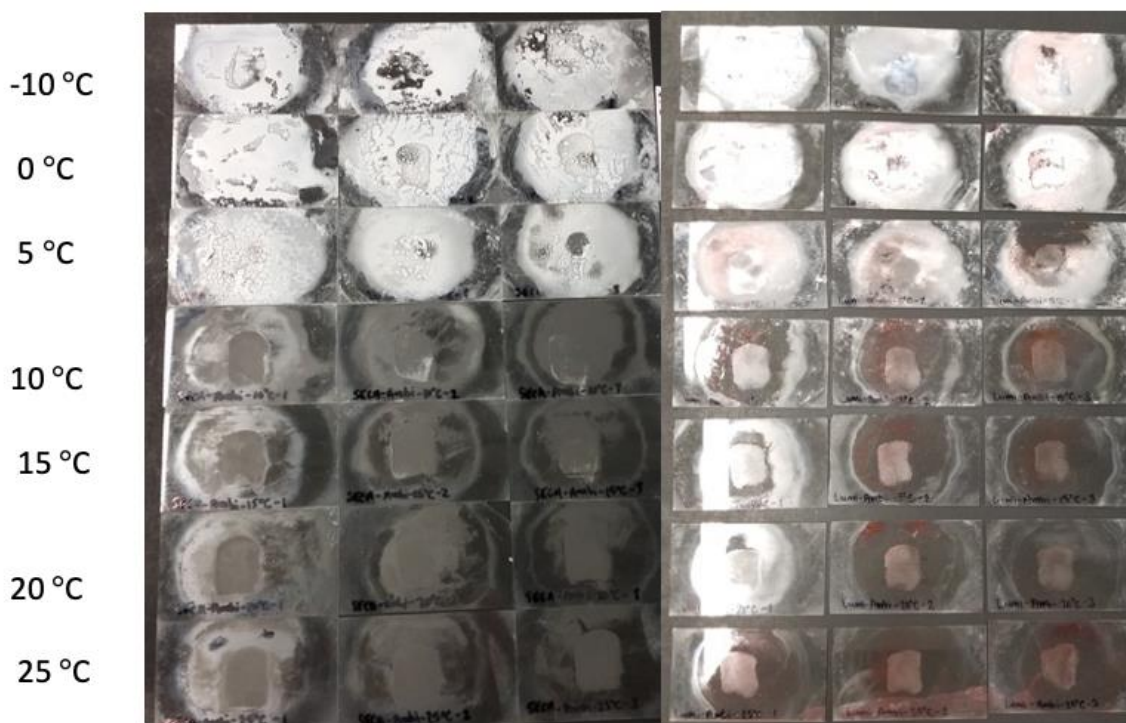


Figure 3-10: Visual appearance of poly (ethyl cyanoacrylate) on fingerprints for surface temperatures from -10 to 50 °C when fuming Sirchie OMEGA-Print (left) and Lumicyano (right) with protocol CFM-HP150 °C-10 m.

polymerization to the point of making the print undetectable. This background polymerization was not as prominent when Lumicyano was fumed using the manufacturer's protocol. Another immediate difference between formulations is the variation in contrast of fingerprint due to the vibrant pink tint of the prints fumed by Lumicyano. The details of the fingerprints are more easily discernable for those fumed by Lumicyano cyanoacrylate than they are for the prints fumed by Sirchie cyanoacrylate. Figure 3-11 shows a close-up of a select print at each surface temperature for both the Sirchie and Lumicyano cyanoacrylates. Prints fumed with Sirchie were photographed under white light and prints fumed with Lumicyano were photographed under white light as well as under fluorescence with an orange filter. The details of the Lumicyano prints are more easily discerned when photographed under fluorescence.

Figure 3-12 shows the average mass of formed PECA on the fumed print after fuming for both formulations as a function of surface temperature. The fuming of both formulations produced similar amounts of PECA on the surface, but Sirchie cyanoacrylate consistently produced more PECA on the substrate than the Lumicyano cyanoacrylate. The amount of PECA produced during fuming is similar for both formulations when the temperature of the fumed substrate exceeds 10 °C. Figure 3-13 shows the molecular weight of the PECA formed on the fumed prints for both the Sirchie and Lumicyano cyanoacrylate formulations, where both formulations form similar molecular weight chains for a given surface temperature. These results therefore show that the presence of the fluorescent dye in the cyanoacrylate formulation does not significantly inhibit the growth of PECA during the fuming process.

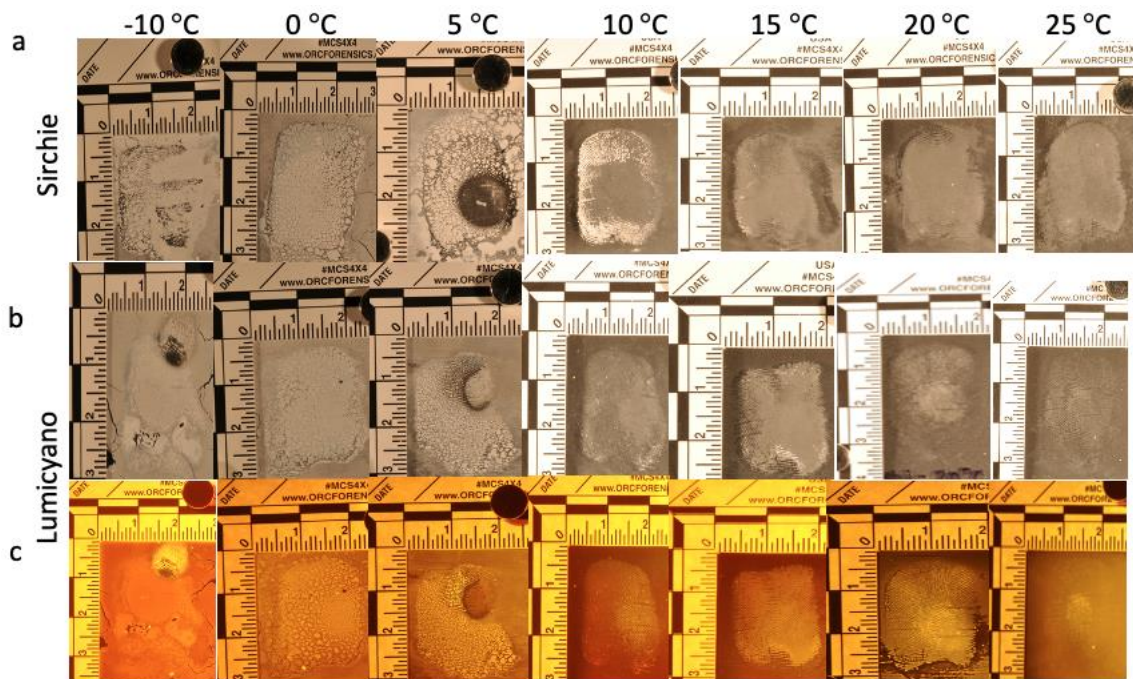


Figure 3-11: Photos of glass slides after fuming over a range of surface temperatures at ambient relative humidity for (a) Sirchie OMEGA-Print under white light, (b) Lumicyano under white light, and (c) Lumicyano under fluorescent light and an orange filter.

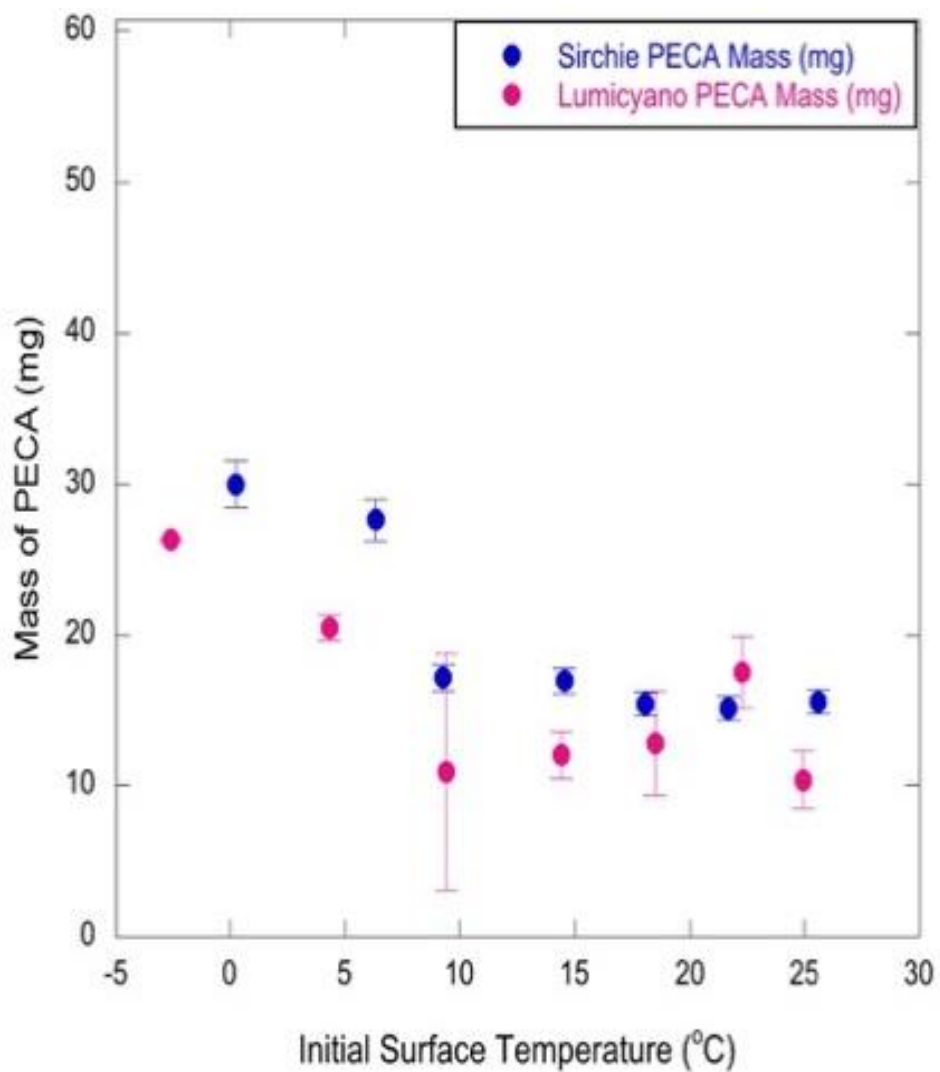


Figure 3-12: Average mass of poly(ethyl cyanoacrylate) on glass slides for surface temperatures from -10 to 25 °C when fuming prints using Lumicyano and Sirchie OMEGA-Print and the CFM-S-HP150 °C-10 m protocol.

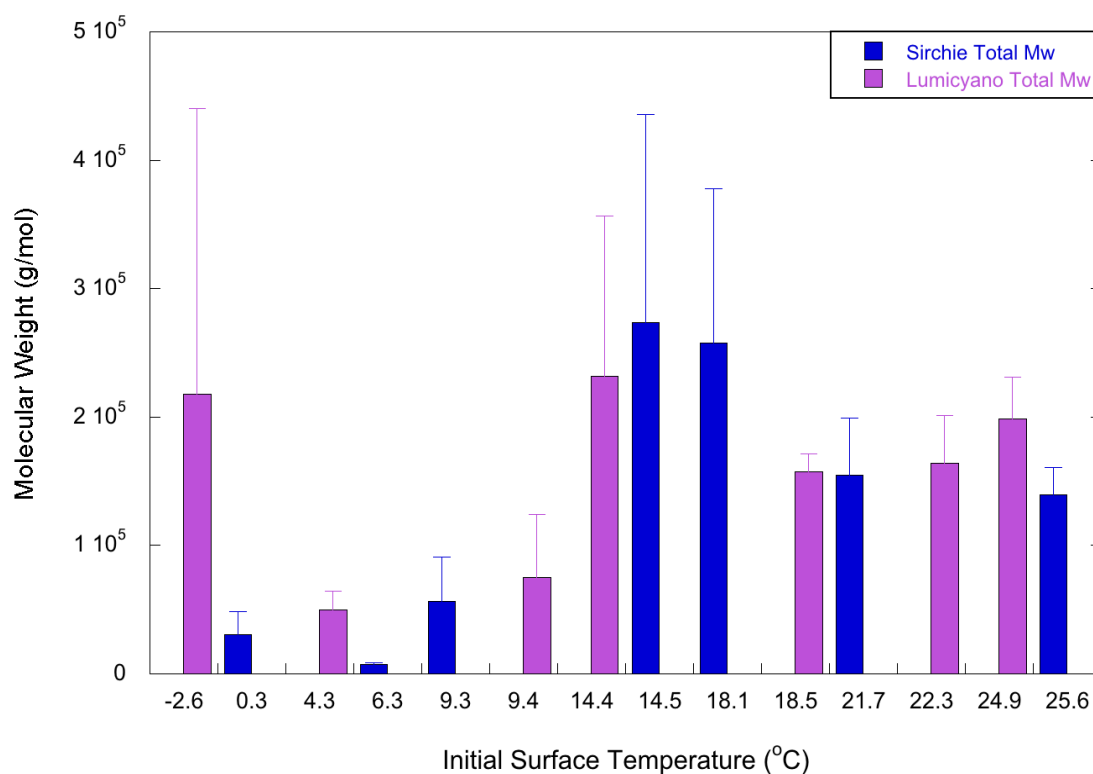


Figure 3-13: The molecular weight of poly(ethyl cyanoacrylate) for surface temperatures from -10 to 25 °C when fuming Sirchie OMEGA-Print and Lumicyano using the CFM-S-HP150 °C-10 m protocol.

The PECA formed from the Sirchie cyanoacrylate creates more chains than those that are formed from Lumicyano, as shown in Figure 3-14, where the difference is most obvious at lower surface temperatures where condensation is observed. Our results from Chapter 2 elucidate how the decrease in surface temperature can lead to moisture collected on the surface of the glass, leading to the formation of shorter and lower molecular weight PECA. Although Lumicyano and Sirchie were fumed under identical conditions, Lumicyano forms similar amount of PECA but fewer chains.

The fluorescent tetrazine is electron withdrawing, which is known to stabilize the negative charge on a carbanion, such as the one that exists at the growing chain end of an anionic polymerizations. This increase in stability could lead to a decrease in reactivity and a slower rate of initiation or propagation. However, the similar mass and molecular weight PECA formed for the two formulations suggest that the tetrazine does not significantly alter the polymerization process. The similarity in mass and molecular weight of PECA formed also translates to comparable integrity of the print, regardless of formulation.

The Coupled Effects of Fuming Time and Formulation on CFM

The variation of the amount of PECA on the surface as well as the larger number of chains produced by fuming Lumicyano with the CFM-L-HP120 °C-20 m protocol relative to when it is fumed with the CFM-S-HP150 °C-10 m protocol is interesting. There are two primary differences between the tested protocols: the hot plate temperature and

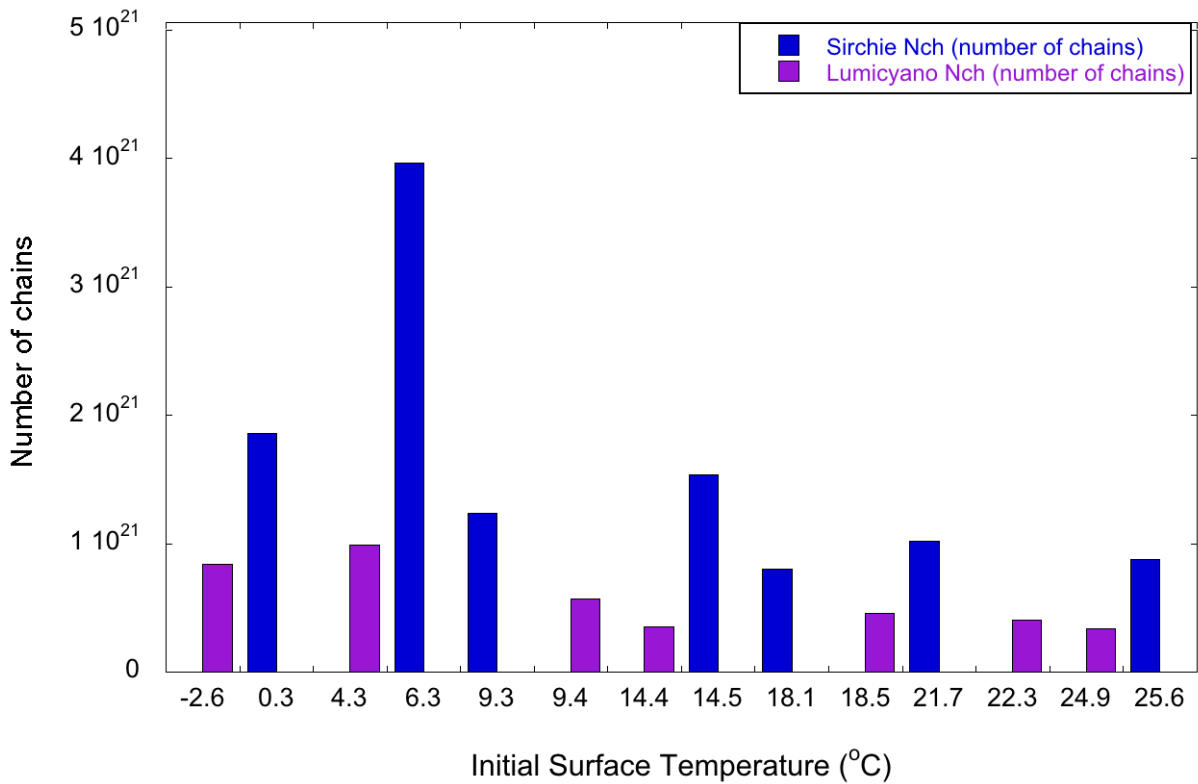


Figure 3-14: The average number of chains (bottom) for surface temperatures from -10 to 25 °C when fuming Sirchie OMEGA-Print and Lumicyano using CFM-S-HP150 °C-10 m.

the fuming time. A higher hot plate temperature should lead to faster vaporization, therefore, faster transport of monomer to the print, which is the reaction site, and faster polymerization.

The longer fuming time of the suggested manufacturer protocol of Lumicyano suggests time plays a vital role in the optimization of fuming with the Lumicyano formulation. To more thoroughly illuminate the importance of the fuming time and connect these studies to the manufacturers protocol, both formulations were fumed at select surface temperatures for 20 minutes by extending the standard Sirchie protocol (CFM-HP150 °C-20 m).

Figure 3-15a shows the amount of PECA formed on prints that are fumed for 20 minutes for both formulations, where both produce a similar amount of PECA, but the Lumicyano formulation produces slightly more PECA than the Sirchie cyanoacrylate. Figure 15b provides the molecular weight of the PECA formed from fuming both formulations at this extended fuming time of 20 minutes. The PECA formed by the fuming of Lumicyano has consistently higher molecular weight than the PECA formed from Lumicyano after ten minutes of fuming. This increase in PECA chain length was not observed with the Sirchie formulation with longer fuming times. Figure 3-15b also shows the molecular weight of the PECA formed on fumed prints, which increases with a decrease in temperature.

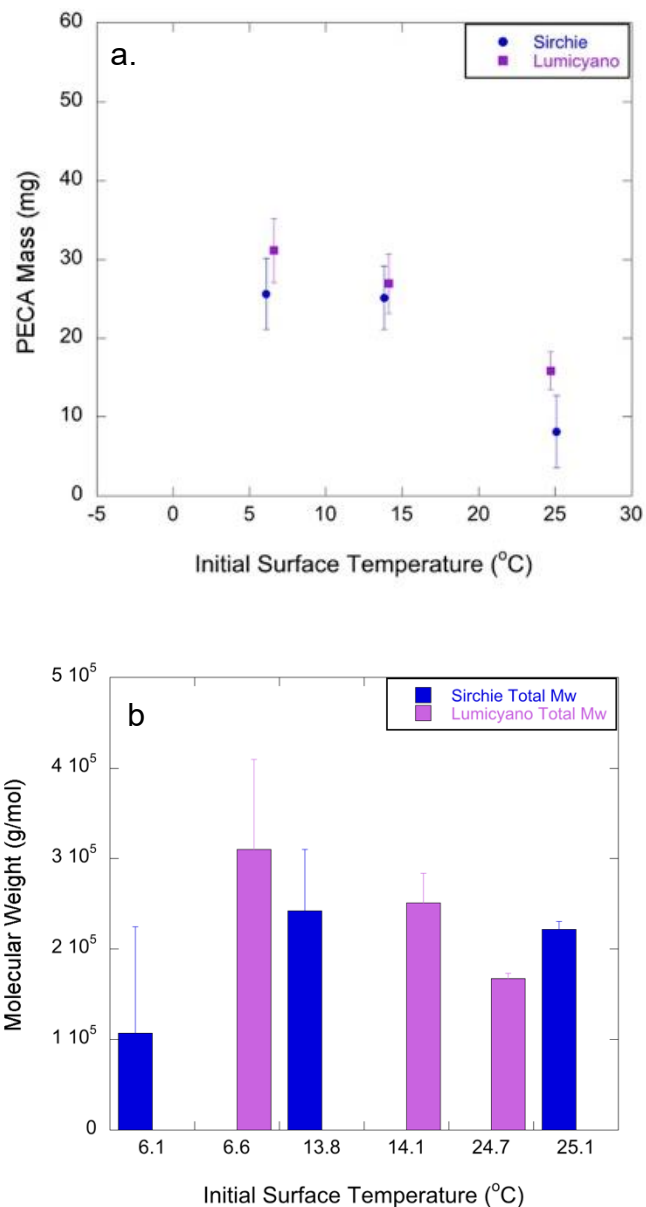


Figure 3-15: (a) Average mass of poly(ethyl cyanoacrylate) for Lumicyano and Sirchie as well as (b) the molecular weight of PECA formed when fuming Lumicyano and Sirchie at select surface temperatures between about 5 and 25 °C at ambient relative humidity. Fuming occurs on a hot plate set to 150 °C with a fuming time of 20 minutes.

At the lowest fumed temperature ($\sim 6^{\circ}\text{C}$), Lumicyano grows more higher molecular weight polymer than Sirchie. To provide further insight into the variation in polymerization that results in the higher molecular weight for Lumicyano, the effect of time on the success of the ECA polymerization during fuming latent prints with Lumicyano is needed.

Time Evolution Studies of PECA formed from the Lumicyano and Sirchie OMEGA-Print formulations using the CFM-S-HP150 °C-20 m protocol

Time studies were conducted to provide insight into the polymerization of the Sirchie and Lumicyano monomers throughout the course of fuming. These studies were completed on surfaces that were kept at 10°C . The fuming times ranged from one to 20 minutes. Figure 3-16a shows the loss of cyanoacrylate from the heated pan as a function of fuming time, where the initial loading of ECA was four milligrams. The hot plate was set to 150°C . This data shows that the Sirchie vaporizes more quickly than the Lumicyano formulation. However, while Lumicyano initially vaporizes more slowly than the Sirchie OMEGA-Print ECA, after exceeding ten minutes of fuming, both formulations have vaporized nearly all of the ECA initially present.

The average mass of PECA formed during the fuming of Sirchie OMEGA-Print and Lumicyano, as shown in Figure 3-16b, which shows a consistent increase in mass of PECA for both formulations as time increases, where both form comparable amounts of PECA. Figure 3-16c and 3-16d document the change in polymer molecular weight and number of chains formed as a function of fuming time for both formulations. Lumicyano

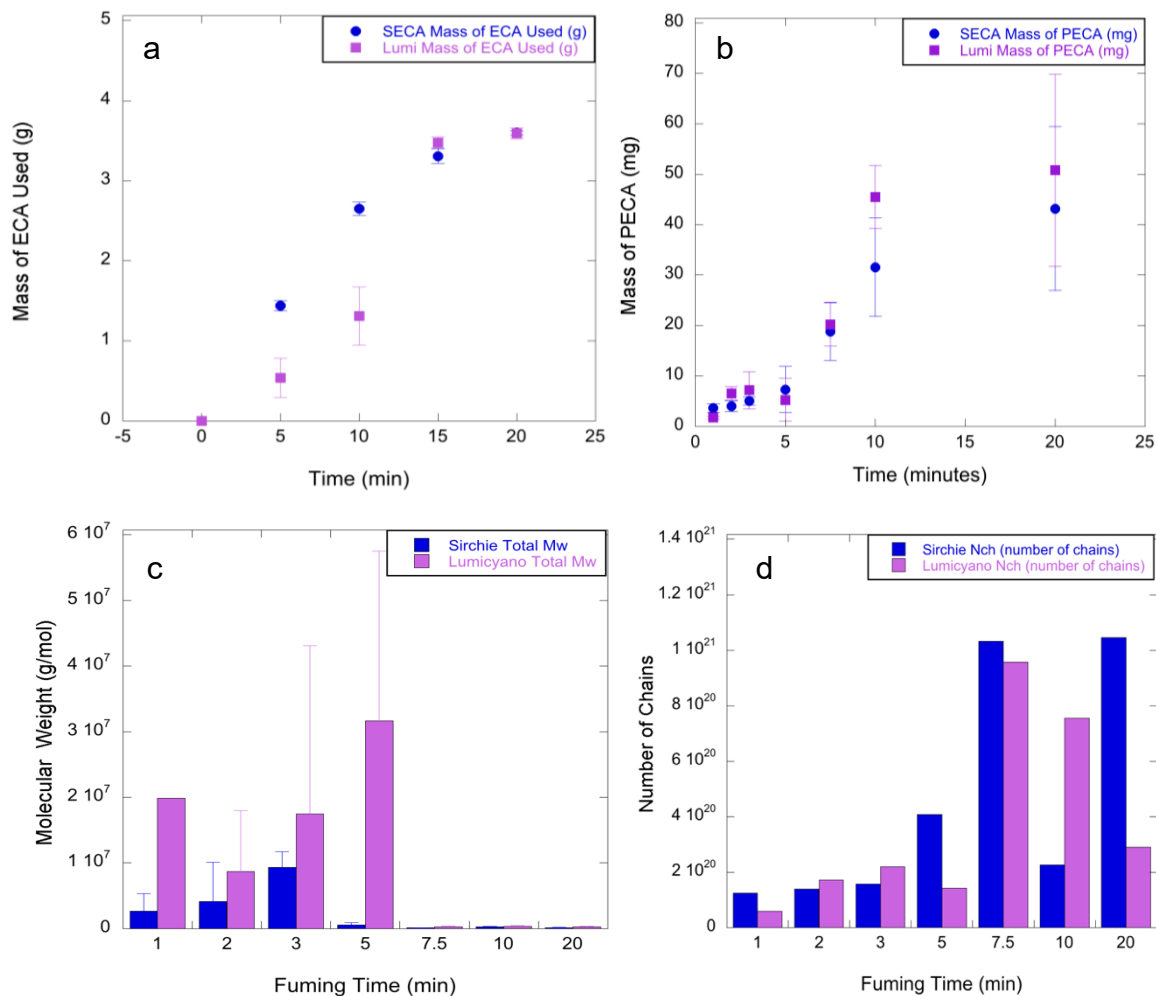


Figure 3-16: (a) Total ECA monomer utilization for each formulation, (b) Average mass of poly (ethyl cyanoacrylate), (c) the molecular weight characteristics of poly(ethyl cyanoacrylate) and (d) the average number of chains on glass slides after fuming at a surface temperature of about 10 °C at ambient relative humidity when Lumicyano (purple) and Sirchie (blue) are fumed under the same conditions up to 20 minutes.

forms significantly larger molecular weight polymer for all fuming times despite having similar amounts of polymer on the surface as Sirchie. Both formulations produce a peak number of chains at seven and a half minutes. The slower vaporization of the Lumicyano formulation causes less ECA vapor to be available for reactions with the fingerprint components. Therefore, the slower vaporization causes a slower initiation on the surface of the deposited fingerprint. As a result, Lumicyano benefits from longer fuming times to allow the complete utilization of all available monomer.

Discussion

The impact of cyanoacrylate formulation on the polymerization of ECA during the cyanoacrylate fuming process is the focus of these studies. The formulations used are Sirchie OMEGA-Print and Lumicyano, where the Lumicyano contains a fluorescent tetrazine. For all fuming protocols, the PECA formed from the fuming of Lumicyano exhibits a vibrant pink color which improves the contrast between the print and the supporting surface. These studies showed the fuming of prints with both Lumicyano and OMEGA-Print produced more polymer at lower temperatures (ca. $< 15\text{ }^{\circ}\text{C}$), in agreement with previous studies.

Prints that were fumed with Sirchie OMEGA-Print ECA monomer using the CFM-S-HP150 $^{\circ}\text{C}$ -10 m protocol produced less PECA than prints that were fumed with Lumicyano using the CFM-L-HP120 $^{\circ}\text{C}$ -20 m protocol. Both formulations show the same impact of surface temperature, where more PECA is formed at lower temperatures. On

average, Sirchie OMEGA-Print produces more chains and lower molecular weight PECA than Lumicyano fumed at 120 °C for 20 minutes. This implies that there are fewer side reactions in the polymerization of the ECA with the Lumicyano formulation than with the Sirchie OMEGA-Print formulation.

To elucidate the importance of fuming time on the production of PECA during fuming, both cyanoacrylate formulations were fumed with the CFM-S-HP150 °C-10 m protocol. The developed prints from the fuming of both formulations had similar visual appearances across all surface temperatures with excessive background polymerization below 10 °C. The PECA grown on the surface of prints fumed with Lumicyano showed greater contrast than those fumed with Sirchie due to the pink hue of the PECA from Lumicyano monomer, allowing for easier observations of the fingerprint ridge details, especially when observed under fluorescent light. Both formulations produced similar quantities of PECA, with the amount of PECA formed from fuming Lumicyano being slightly lower, but with similar molecular weight PECA. However, the PECA grown from fuming the Sirchie formulation appears to form more chains than the PECA formed from fuming the Lumicyano formulation. This is consistent with the interpretation above that the propagation of the Sirchie formulation is more prone to termination or side reactions, producing more polymer chains. It is interesting that the amount of polymer formed from the Sirchie formulation is slightly higher than Lumicyano, which could be the result of a more efficient initiation of the chain growth.

The overdevelopment observed when fuming prints with Lumicyano using the CFM-S-HP150 °C-10 m protocol was more prominent than when fumed with Lumicyano

using the CFM-L-HP120 °C-20 m protocol. This suggests a faster polymerization at the higher vaporization temperature and is interpreted to be the result of the more rapid vaporization of the ECA monomer, and thus transfer of more monomer to the print, at the elevated temperature. Additionally, the average mass and molecular weight of PECA grown from prints that were fumed with the Lumicyano monomer were larger when the CFM-L-HP120 °C-20 m protocol was utilized. Thus, the polymerization time impacts the chain length and amount of polymer formed. This is also consistent with a polymerization that is less susceptible to side reactions, where the longer reaction time results in more propagation, and fewer, longer chains.

To further understand the impact of fuming time on the polymerization of PECA during fuming, prints were fumed for 20 minutes with both the Sirchie and Lumicyano formulations at 150 °C (CFM-S-HP150 °C-20 m). Both formulations produced similar amounts of PECA, where the amount of polymer increases with the fuming time for both formulations at ~15 °C. However, the amount of PECA formed at ~6°C and 20 min fuming is significantly higher than 10 min fuming for the Lumicyano formulation, but the amount of PECA formed from the Sirchie formulation does not change much with longer fuming time. Thus, Lumicyano benefits from a longer fuming time while Sirchie produces a similar amount of PECA regardless of fuming time. This is again consistent with a dominant propagation reaction in the Lumicyano polymerization, but a polymerization that is susceptible to termination and side reaction in the Sirchie polymerization.

Time evolution studies of both the Lumicyano and Sirchie OMEGA-Print revealed Lumicyano vaporizes more slowly than Sirchie OMEGA-Print. In spite of a slower

vaporization, Lumicyano still produces a similar amount of PECA as Sirchie when fumed over a range of fuming times, and forms PECA with higher molecular weight than Sirchie. This is interpreted to indicate that the growth of the Lumicyano chain occurs with less susceptibility to side reactions, where the polymerization mechanism is dominated by the propagation of the growing polymer chain.

The tetrazine molecule has a strong, positive quadrupole moment and a high molecular polarizability, and have been shown to complex with anions⁵⁸ or cations.⁵⁹ The anion complex relies on anion- π interactions, while tetrazine-cation complexes are characterized by low energy electron or charge transfer phenomena.⁶⁰ Thus, the tetrazine can readily complex with the ion pair at the end of the growing polymer chain. The decrease in susceptibility of the Lumicyano growing polymer chain to side reactions may, therefore, be the result of the fluorescent tetrazine coordinating loosely at the growing chain end. The presence of this complex may act as a 'protecting group' for the reactive chain end, similar to protecting groups that are found in controlled radical polymerizations (Figure 3-17). In this proposed mechanism, the bulky tetrazine inhibits side reactions and slows, but does not stop, propagation, in agreement with the results reported above. Further experiments are needed to verify this mechanism.

Conclusion

Lumicyano is a promising ethyl cyanoacrylate formulation for fingerprint fuming, which enable a one-step alternative to unmodified ECA. Fuming Lumicyano achieves

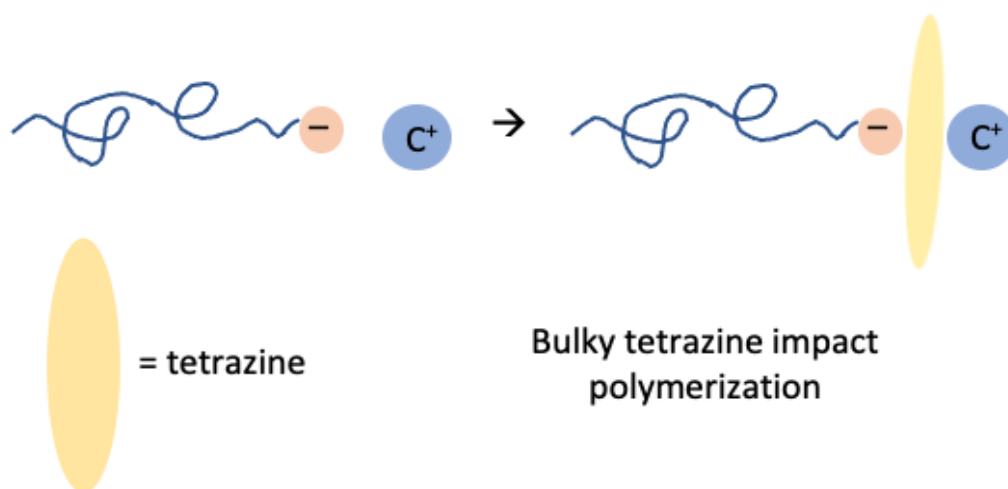


Figure 3-17: Illustration of possible complexation of tetrazine with the anion or cation at the end of the growing polymer chain

comparable development of the print under the same fuming parameters but has the benefit of having a vibrant pink color which improves the contrast with a wide variety of deposition surfaces and this contrast can be further enhanced with fluorescent light. On a molecular level it appears that the presence of the fluorescent tetrazine does impact the polymerization of the ethyl cyanoacrylate in the open environment of fuming. The results presented in this work indicate that the polymerization of the Sirchie formulation, in general, creates a similar amount of PECA as the Lumicyano formulation for a given set of fuming conditions. However, the molecular weight of the resultant PECA is usually less and the number of chains is more than that formed by fuming Lumicyano under similar conditions. This is interpreted to indicate that the polymerization mechanism of the Sirchie formulation is more susceptible to termination and side reactions that interrupt chain growth, while the polymerization of the Lumicyano formulation is less susceptible to these side reactions and is dominated by the propagation reaction. One possible molecular level explanation for this observation is that the fluorescent tetrazine interacts with the ion pair at the end of the growing polymer chain, inhibiting side reactions and allowing efficient chain propagation.

CHAPTER 4 : THE EFFECT OF SUBSTRATE ON THE FUMING OF LATENT PRINTS BY THE CYANOACRYLATE FUMING METHOD

Abstract

A prevalent method in forensics to reveal latent prints on surfaces is the cyanoacrylate fuming method (CFM). The CFM is governed by the reaction of ethyl cyanoacrylate (ECA) with biological components that exist in fingerprints. These biological components serve as initiators for an anionic polymerization of the ECA. There are a variety of surfaces on which fingerprints can be revealed at crime scenes. In order to gain a more in-depth knowledge of how the polymerization of ECA is affected by surface type, the CFM was conducted at select surface temperatures on fingerprints that are deposited on glass, brass, and polyethylene terephthalate (PET), materials that mimic common surface types on which evidence is found. The amount of poly(ethyl cyanoacrylate) (PECA) and its molecular weight formed on the surfaces by the CFM were analyzed for each substrate. The amount of PECA polymer formed on glass was comparable to that formed on PET. Contact angles of all three surface types show that the glass is the most hydrophilic surface, while brass is the most hydrophobic. Since our previous studies proved surface temperature plays a vital role in the polymerization of the ECA during fuming, the thermal behavior of each surface was also considered as a factor in polymerization success. Ultimately, the wettability (or hydrophilicity) of each surface to water was found to have the greatest influence on the success of the polymerization of ECA. As glass is the most hydrophilic surface studied, water is more likely to be present on the surface. We interpret the results to indicate that the presence of water on the glass surface acts to inhibit the chain growth in the anionic polymerizations of ECA, resulting in a lower amount of PECA formed during fuming on this substrate. Similarly, the brass as

most hydrophobic tolerates the presence of water the least, and thus the polymerization of ECA on this surface is less encumbered and more successful. Thus, the wettability of a surface and the propensity for water to reside on the surface appears to be the overarching factor in impacting the success of the ECA polymerization reaction that governs the cyanoacrylate fuming mechanism. This study, therefore, offers fundamental insight to the forensic community as it relates to variations in the molecular level processes that govern the fuming process of latent prints on different surfaces.

Introduction

The cyanoacrylate fuming method is a technique utilized by forensic scientists and crime scene investigators to visualize latent fingerprints in the lab or at the crime scene. This method is based on the anionic polymerization of the monomer, ethyl cyanoacrylate (ECA). In this process, the ECA monomer is heated, and its vapors interact with the components of fingerprint residue. These components consist of amino acids, fatty acids, lipids, and cholesterol, among others.³ Water plays an important role in the polymerization due to its solvating effects on the zwitterionic constituents in fingerprint deposits.⁶¹ As the monomer vapors polymerize from the print, a white polymer, poly(ethyl cyanoacrylate) (PECA), forms on the surface of the fingerprint. Thus, the latent print, which is initially difficult to see with the naked eye, is now readily visible and may be analyzed by forensic experts. Post-fuming, the print is typically photographed for further analysis and may be tested for DNA.

There are a variety of different surfaces which can be encountered at a crime scene, such as plastic, paper, or metal. Anecdotal observations indicate that the chemistry of the surface on which the print resides can have a significant impact on the success of the CFM to develop the print. A major consideration is whether there is competitive or preferential initiation of polymer growth on the fingerprint surface or the surface on which the print is deposited. Stoehr et al. showed the hygroscopic nature of fingerprint residue, which is attributed to the presence of salt in sweat. Interestingly, their findings also elude to a preference of water condensation on the hydrophobic sebum

components in fingerprints before condensing on hydrophilic surface upon which the print may rest.⁶²

Previous studies have examined the role of a supporting surface on the CFM method. For instance, The diffusion of fatty acids and triglycerides within the ridges of fresh prints and prints aged for 24 hours on four different surfaces (plain glass, glass treated with water repellant, stainless steel, and PET-scotch tape) were studied.³ Fatty acids and triglycerides have very different polarities, where the variation in polarity correlates to the diffusion rate of the compounds. The contact angle of each surface was also measured, showing the following trend: plain glass (40.6°), stainless steel (68.3°), PET (70.5°), and treated glass (101.7°). Generally, any surface with a contact angle above 90° is considered hydrophobic and any surface with an angle below 90° is hydrophilic. O'Neil and Lee considered stainless steel and PET as partially hydrophilic. Their findings indicate the diffusion of the fatty acids and triglycerides were dependent on the hydrophobicity/hydrophilicity of the surface with nonpolar triglycerides diffusing slower and with limited interaction with the surface, while the fatty acids diffuse more readily and interact more with the surfaces due to its polar carboxyl groups.³ Interestingly, the fatty acid compounds diffused more readily on PET, where the fatty acids completely diffused from ridge to valley of the print. This is in spite of the fact that PET has a similar contact angle to the stainless steel. This behavior is attributed to the potential variation of PET structure to modest heating (~ 55°C) that is not relevant to metal and glass. This indicates that the temperature is impact of the surface on the diffusion of fingerprint constituents. As CFM is initiated by the components in fingerprint residue, the diffusion of those

compounds along the surface may impact the success of the polymerization of the PECA on the substrate relative to the polymerization from on the fingerprint ridges.

Most widely utilized polymers are insulators. Glass is likewise an insulator and metals, such as copper, are much more thermally conductive.⁶³ The effectiveness of the most common latent print visualization methods for nonporous surfaces were also examined on three metals, bronze, brass and stainless steel. In this study, cyanoacrylate fuming showed superior performance on brass and bronze with over 60% of the prints exhibiting identifiable detail.⁶⁴ Deposited fingerprints on stainless steel were more difficult to visualize, which is ascribed to the spreading of the fingerprint compounds into the semi-porous oxide coating of the metal.

An aspect of fuming on plastic surfaces which needs to be considered is that many commodity plastics contain a range of additives that tend to collect near the surface.¹² These additives alter the surface chemistry of the plastic and therefore, have the potential to impact the deposition of fingerprint as well as the polymerization of ethyl cyanoacrylate during fuming. Investigations that monitored the success of the CFM on aluminum, copper, glass, polyethylene (PE), and steel emphasize the importance of the temperature of the surface, and its specific heat, in the fuming process.²⁹ The specific heat of a substance quantifies the energy required to increase the temperature of the substrate. Thermal conductivity describes the speed of the energy transfer. In these studies, an ideal surface processing temperatures was defined for each of the substrates tested. These results indicate that a surface with a higher heat capacity deposited more PECA on the surface of the fingerprint.^{25, 29, 65} More precisely, fuming temperatures that are

approximately 5 – 20° C below room temperature formed PECA that resulted in improved visualization of the fingerprint. However, based on these observations, the ideal processing temperature did not correlate strongly with the specific heat capacity of the surface. Therefore, there are other surface-related factors that impact the cyanoacrylate fuming process.

In another study, Mankidy et al found the number of initiation sites on a modified glass substrate correlate to the wettability of the ethyl cyanoacrylate monomer on the surface. If there is low wettability for ECA, there are less initiation sites and vice versa. This lower number of initiation sites results in a slower initiation. Furthermore, the presence of water is important in the polymerization of PECA, as it solvates the ion pairs of the fingerprint components that serve as initiators. This, increases the overall rate of polymerization as the ion pairs are more easily accessible. However, too much water on the surface may inhibit the polymerization as water can cause chain termination for the anionic polymerization.⁶¹ Thus, the hydrophilicity/hydrophobicity of the surface must be considered in these studies.

In this work, we examine how the formation of the PECA polymer in the CFM process is affected by the nature of the surface, where glass, brass, and poly(ethylene terephthalate) (PET) are examined at select temperatures and ambient relative humidity. Each surface being tested represents different types of surfaces, i.e. metal, plastic, and glass that may be found at a crime scene. These studies will document how the accumulation of PECA as well as its molecular weight properties are affected by the type of surface on which a fingerprint is deposited. Surface temperature is a major component

of our studies; thus we will also see how the molecular weight and distribution of the PECA formed varies with surface type and surface temperature. These results will be correlated to the properties of the surfaces, including hydrophilicity and thermal conductivity. Interpretation of these will offer a level of understanding of the dominating factor which alters the polymerization for each surface, leading to insight of how the progression of the anionic polymerization of ethyl cyanoacrylate changes with different deposition surfaces. Ultimately, this will provide the forensic community with information and supporting data to tailor and understand the parameters of CFM for optimum visualization of prints based on surface type.

Experimental

Print Deposition

Multiple prints from a single donor were used for the deposition of latent fingerprints on glass slides. In order to produce the most consistent print composition as possible, the following steps were taken to reproducibly deposit prints onto the surfaces: First, hands of the donor are washed with non-fragrant liquid soap for 10 minutes. The hands are then air-dried. Once the hands are dry, the finger is rubbed against an oily area of the face, such as forehead or nose. A print is then deposited by lightly rolling the finger across the surface.

Cyanoacrylate Fuming Method for Variable Surface Temperature

To aid in the understanding of the set-up of these experiments, the apparatus is shown and labeled in Figure 4-1. This environment allows for a single fuming protocol in which a hot plate (A) set to 150 °C is used to vaporize the Sirchie OMEGA-Print formulation of ethyl cyanoacrylate monomer in an Aluminum dish (B) for a fuming time of 10 minutes. To control the surface temperature of the substrate (C), a copper block (D) attached to an Isotemp 3016 temperature controller (E) was placed on the back of the substrate which is attached to a ring stand. The surface temperatures were measured pre- and post-fuming utilizing an infrared thermometer (F). The surface temperatures studied provide a representation of results between -10 and 25 °C. The fuming experiments were completed at ambient relative humidity. The relative humidity was monitored using a hygrometer (G) throughout the fuming process. Fingerprints were fumed with this apparatus on the following substrates: glass, polyethylene terephthalate, and brass. Brass and PET were cut to mimic the dimensions of the glass slide surfaces, which was about 2 by 3 inches.

Gel Permeation Chromatography

The PECA that forms on the fumed prints was removed from the print by sonicating in tetrahydrofuran (THF) for ten minutes to dissolve the PECA. Subsequently, the samples were analyzed via gel permeation chromatography to obtain molecular weight and molecular weight dispersity data of the resulting PECA from fuming on different

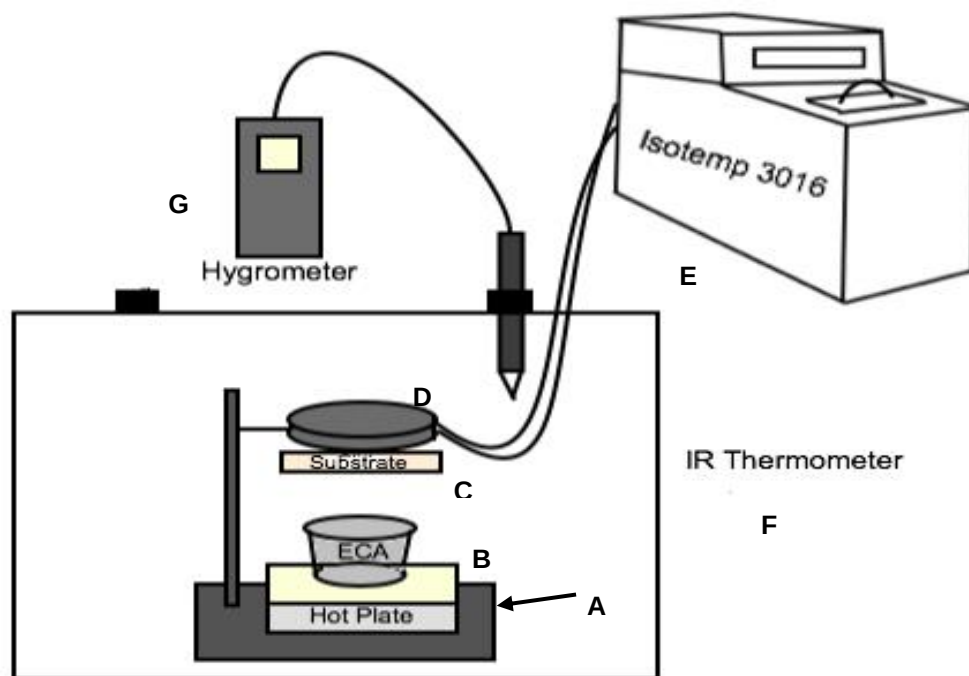


Figure 4-1: Labeled apparatus for performing the cyanoacrylate fuming method (CFM) on glass, PET, or brass (each represented by C).

surfaces at varying temperature. Gel permeation chromatography was carried out utilizing a Tosoh Bioscience EcoSEC instrument equipped with two cross-linked poly(styrene/divinylbenzene) columns. The flow rate was 0.35 mL/min at a temperature of 40 °C with a polystyrene calibration and a refractive index detector, which varies based on the presence of polymer in the THF. The total retention time observed for all samples was 15 minutes.

Attenuated Total Reflection (ATR)-Fourier-Transform Infrared (FTIR) Spectroscopy

A Nicolet iS50 FT-IR Spectrometer was utilized in ATR mode to measure the spectra of the surfaces over wavenumbers within the 5000-400 cm^{-1} region. This experiment is implemented to identify the presence of functionalities and potential contaminants on the surface of PET, glass, and brass.

Contact Angle Measurement

The contact angles of deionized water on the surface of glass, PET, and brass were acquired through the use of a Ramé-Hart NRL C.A. Goniometer Model 100-00¹, shown in Figure 4-2. The user is positioned on the right side of Figure 4-2, near the eyepiece. Before initiating measurements, the eyepiece of the microscope and stage are positioned to center and focus the lens of the microscope with the water drop and surface. The micro-syringe dispenses a drop of water onto the specimen stage. The drop is

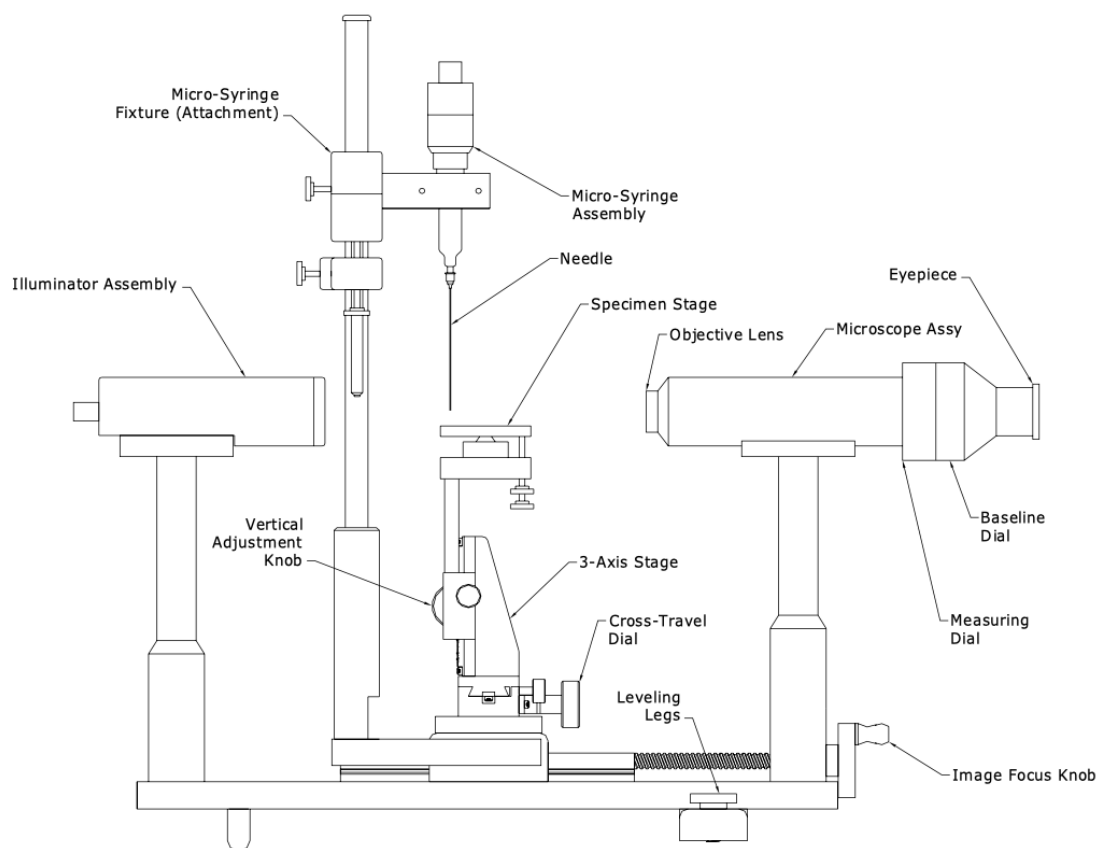


Figure 4-2: Schematic diagram of the Ramé-Hart NRL C.A. Goniometer Model 100-00¹.

illuminated via the light source found adjacent to the eyepiece and the specimen stage. The contact angle of water on each surface is recorded from this view. The reported results are the average of at least three measurements across the surface.

Results

Cyanoacrylate Fuming Method on Multiple Substrates

Fingerprints on glass, polyethylene terephthalate (PET) or brass were fumed with Sirchie OMEGA-Print as the cyanoacrylate formulation over a range of surface temperatures. Each substrate serves as a possible surface which may be encountered at crime scenes. Figure 4-3 depicts the average mass of PECA that is formed on each monitored surface as a function of surface temperature. The fingerprints on the glass and brass surfaces produced similar amounts of PECA while the fingerprints on each surface formed the most amount of PECA on the fingerprints between the surface temperatures of 5 and 10 °C.

Gel permeation chromatography (GPC) was used to assess the molecular weight characteristics of the PECA polymer formed on each substrate. The GPC results plotted as the number average molecular weight (M_n) and weight average molecular weight (M_w) of the PECA formed on each substrate are shown in Figure 4-4 with each surface plotted individually for easy comparison between samples. These results indicate that the brass and glass produce similar trends, showing an increase in molecular weight with increased surface temperature. Although following a similar trend, the PECA formed on brass is

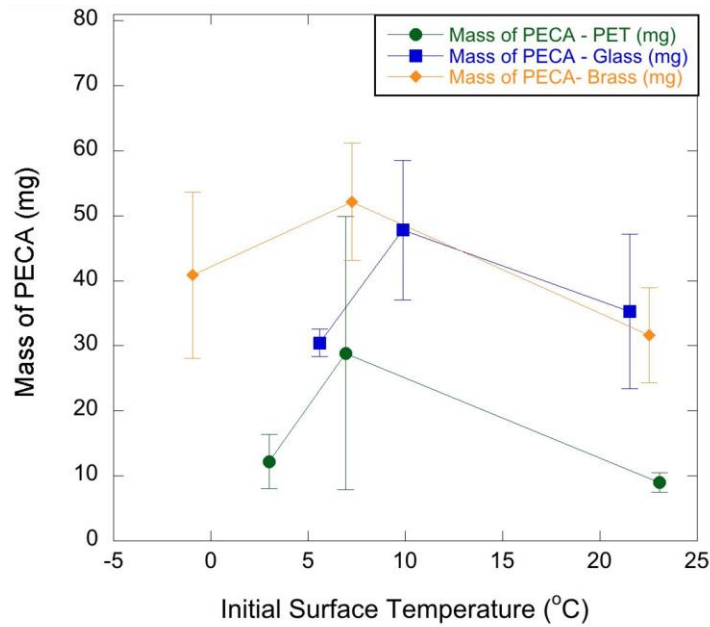


Figure 4-3: Average mass of poly(ethyl cyanoacrylate) on brass, glass, and PET after fuming at surface temperatures ranging from -10 to 25 °C at ambient relative humidity.

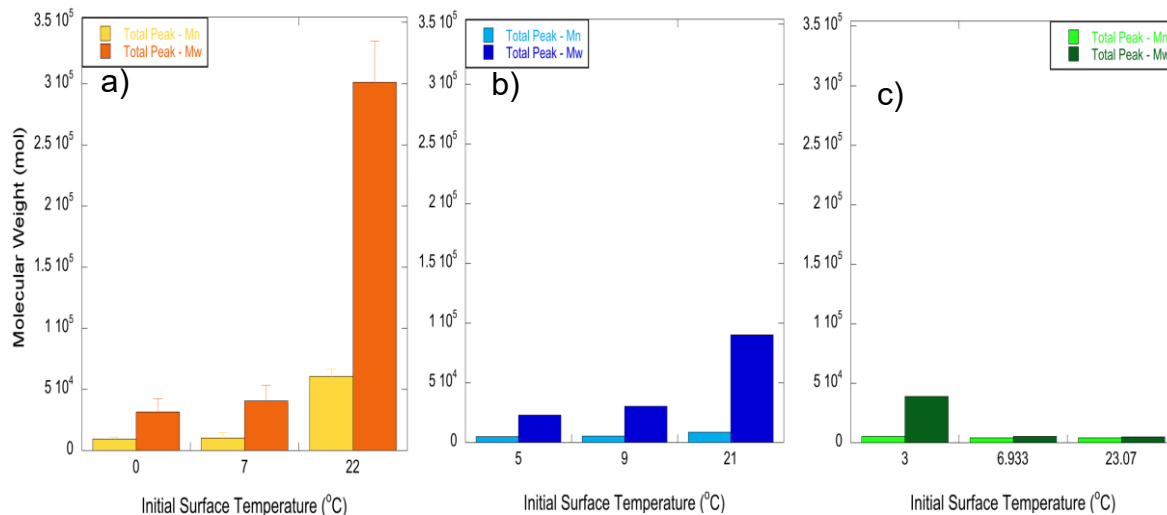


Figure 4-4: Average molecular weight of poly(ethyl cyanoacrylate) on a) brass, b) glass, and c) PET after fuming at surface temperatures ranging from -10 to 25 °C under ambient relative humidity.

much larger, about three times higher average molecular weight PECA than glass. The PECA formed on PET is the lowest molecular weight for all surface temperatures, with the highest molecular weight polymer formed on PET at the lowest observed surface temperature. This suggests the polymerization of ECA on PET proceeds in a different manner than it proceeds on brass and glass.

ATR-FTIR Results

To investigate the impact of surface chemistry on the polymerization of PECA on the surfaces of interest, ATR-FTIR spectroscopy was performed on all samples to observe the presence of any functional groups on the surfaces. The IR spectra of all three samples are provided in Figure 4-5 with all three surfaces being analyzed after washing with acetone and fifteen minutes in the UVO cleaner to remove organic contaminants from each surface. An additional spectrum is present of the brass surface that includes a wash with THF, which was incorporated into the preparation of the brass surfaces to remove any contamination when the brass was cut to size.

The brass and glass slide show no signature of organic contaminants, where the spectra of the brass curve show no IR absorbance across the whole spectrum and the glass slide only shows peaks in the fingerprint region. These peaks (~ 760 and 910 cm^{-1}) are associated with the Si-O or Si-O-Si bonding of the silicon and non-bridged fractured Si-O bonds present in the glass.⁶⁶ The PET IR curve follows the reported IR curve of neat PET, with peaks in the fingerprint region that correspond to a variety of -C-H bonds as

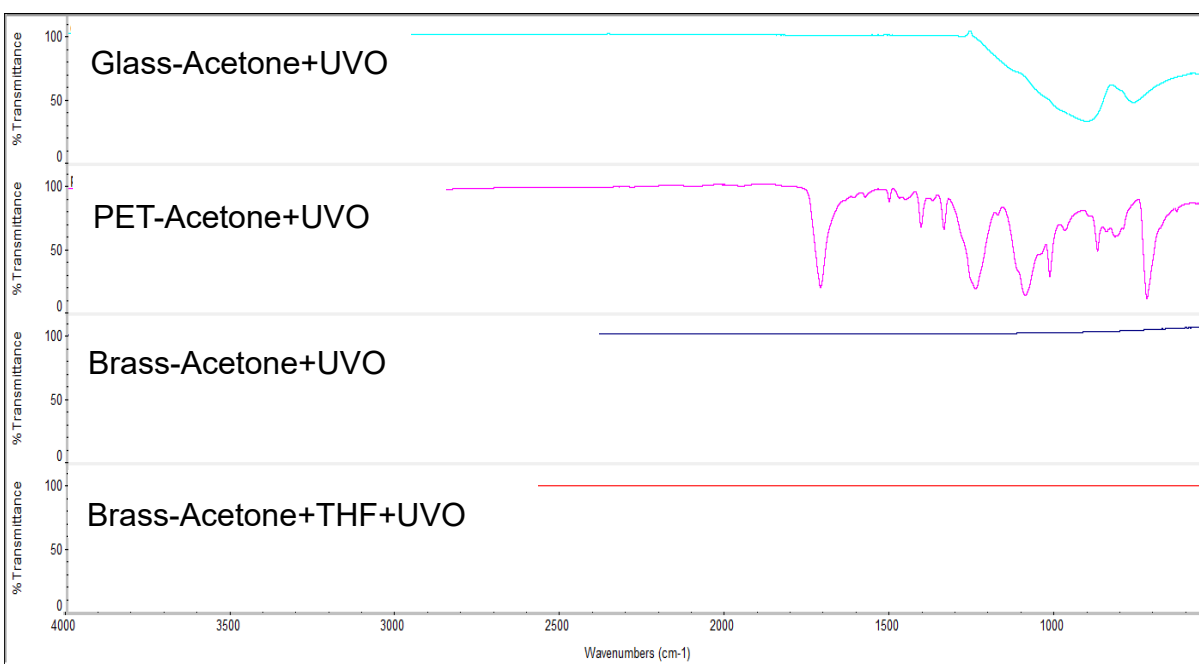


Figure 4-5: ATR-FTIR spectra of all three surfaces including method of cleaning surface before print deposition

well as the carbonyl of the ester at $\sim 1750\text{ cm}^{-1}$.⁶⁷ Thus, the IR data does not show evidence of significant contaminants on these surfaces and the PET, unsurprisingly, contains more functionality than the glass or brass.

Water Contact Angle

The hydrophilicity/hydrophobicity of a surface is well characterized by the contact angle of water on each surface. If the surface is wettable by water, it is considered hydrophilic and if it is non-wettable by water, it is hydrophobic. For a hydrophilic surface, the water spreads across the surface leading to a smaller contact angle (contact angle is $< 90^\circ$) while the water will not spread on a hydrophobic surface (contact angle is $\geq 90^\circ$).⁶⁸⁻
⁷⁰ The previously reported contact angles of each surface are shown in Table 4-1.^{71, 72}

The previously reported water contact angles of brass and PET are similar, however our results do not find this to be true for our samples. As seen in Table 1, the water contact angle of brass is higher than previously reported values, which could be the result of variations in its processing, such as an application of any coatings or polishing. Glass has a slightly lower average contact angle than previously reported. PET's experimental average contact angle is similar to previously reported values.

The roughness of a surface can also impact the measured water contact angle, where any scrubbing or rubbing of the surface, such as when cleaning or polishing, can increase the roughness.^{68, 69} For example, if the surface is hydrophilic, increased surface

Table 4-1: Water Contact Angle for Brass, Glass and PET Surfaces

Surface	Reported contact angle (°)	Measured Contact Angle (°)			Average Contact Angle (°)
		1	2	3	
Brass	~73 ⁷²	93.9 ± 5	93.9 ± 5	93.0 ± 5	93.6 ± 5
Glass	~25 ⁷²	14.9 ± 5	16.9 ± 5	21.1 ± 5	17.6 ± 5
PET	72.5 ⁷¹	76.1 ± 5	75.9 ± 5	75.1 ± 5	75.7 ± 5

roughness will decrease the contact angle further making the surface more hydrophilic. This is understood to be related to the increased surface roughness that increases the surface area, leading to a more hydrophobic surface.⁶⁹ Therefore,, the cleaning protocol detailed in the experimental section, which involved scrubbing and rubbing is the most likely cause of the difference of our reported values from previously reported values.

The measured contact angles indicate that the brass is hydrophobic, which indicates that water does not spread on the surface. Since water can serve as a terminating or chain- transfer agent in anionic polymerizations, this suggests that the hydrophobicity of the surface inhibits the presence of water at the surface. This in turn, results in less termination in the PECA polymerization on brass, contributing to the higher molecular weight PECA, as seen in Figure 3. However, the hydrophilicity of the surface does not appear to be controlling the molecular weight of the polymerized ECA for the PET and glass surfaces, as the PET is more hydrophobic than the glass, yet lower molecular weight PECA is formed on the PET than on the glass.

Evaluation of Fingerprint Deposition on Surfaces

The composition of the surface may also impact the amount of fingerprint residue that remains on the surface after deposition, which in turn can impact the number of initiators present and therefore the polymerization process. With this in mind, the mass of fingerprint deposited on the brass, glass, and PET surfaces was monitored. Figure 4-6 plots the average amount of fingerprint residue that resides on each surface before

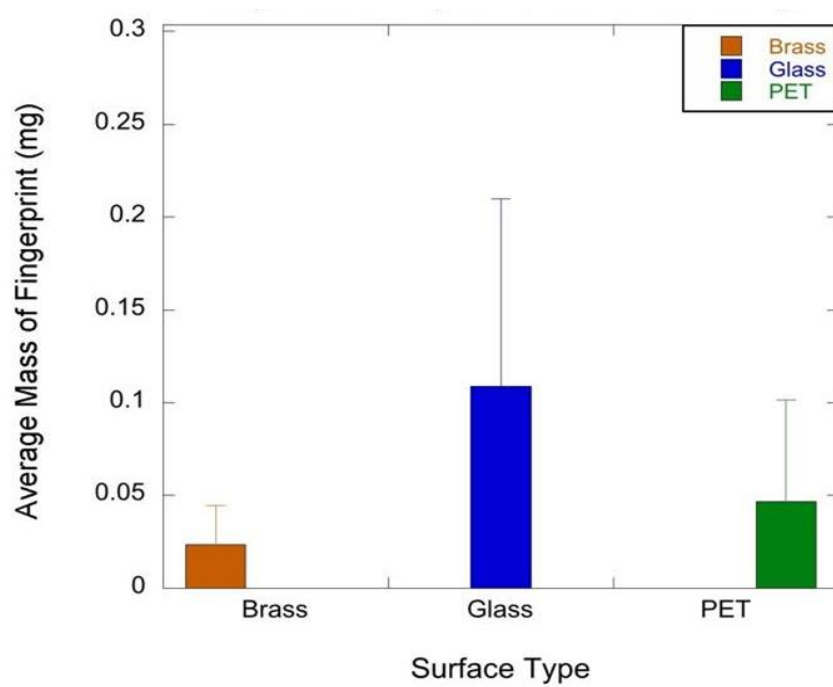


Figure 4-6: Average mass of fingerprint on each surface.

fuming. This plot shows that amount of fingerprint residue varies significantly with surface, and therefore normalizing the mass of PECA that is formed on fuming to the amount of fingerprint residue offers a more accurate depiction of the impact of the surface on the polymerization process. In order to normalize our results to the amount of fingerprint residue on the glass surface, the mass of the PECA formed on brass was multiplied by 4.5 and the mass of PECA formed on PET was multiplied by two.

Determination of Multiplication Factors for Surfaces:

$$\text{Average Fingerprint Mass on Brass} \times (\text{ratio}) = \text{Average Fingerprint Mass on Glass}$$

$$(\text{ratio}) = \frac{\text{Average Fingerprint Mass on Glass}}$$

$$\text{Average Fingerprint Mass on Brass}$$

$$\text{Average PECA Mass of Brass} \times (\text{ratio}) = \text{Normalized Ave. PECA Mass of Brass}$$

The normalized mass of PECA formed on each surface as a function of surface temperature is plotted in Figure 4-7. This shows that when accounting for the variation in amount of fingerprint residue, the fingerprints on the glass and PET form similar amounts of PECA on the surface. However, the fingerprint on the brass surface creates significantly more PECA than the other two surfaces. Thus, the propensity of the surface to retain the fingerprint residue appears to contribute to the amount of polymer that grows on a fingerprint as a result of the CFM process.

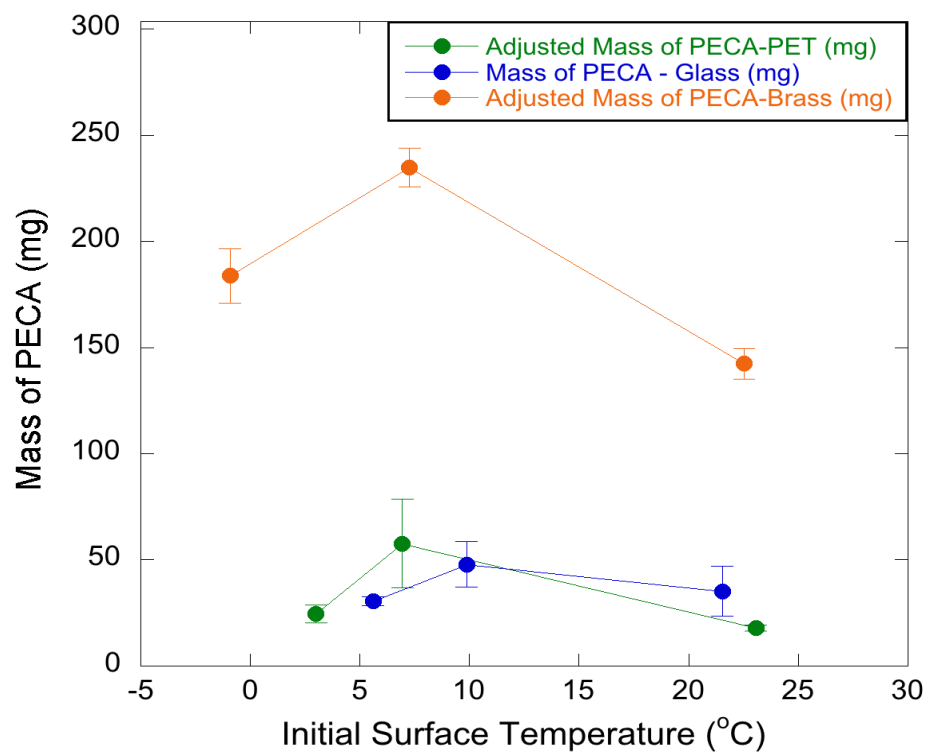


Figure 4-7: Normalized average mass of poly(ethyl cyanoacrylate) on brass, glass, and PET after fuming at surface temperatures ranging from -10 to 25 °C at ambient relative humidity.

Impact of Thermal Conductivity of the surface

Previous research in our laboratory has shown that surface temperature impacts the polymerization of ethyl cyanoacrylate and the thermal properties of the surfaces may impact the success of the polymerization reaction.⁵² The thermal conductivity of the surfaces will impact the temperature of the surface during fuming, and any variation in actual surface temperature will influence the polymerization. Previous studies report that the thermal conductivities of brass, glass and poly(ethylene terephthalate) are 109.0, 0.8 and between 0.15 and 0.4 Watts per meter Kelvin (w/m K), respectively.⁷³⁻⁷⁶ Figure 4-8 shows the change in surface temperature during the fuming process as a function of the initial surface temperature (°C) for these three surfaces. These results correlate well to the thermal conductivities of the surfaces, where the brass shows very little change in temperature during fuming because the copper block that controls the temperature of the surface transfers heat more readily during the fuming process. Similarly, the PET surface shows a larger variation in temperature, which is consistent with the limited heat transfer from the copper block through the PET Film due to the lower thermal conductivity. These variations, however, do not appear to correlate to the success of the polymerization reaction, as the temperature of the surface during the printing process does not vary significantly among the three surfaces, certainly not enough to explain the data in Figure 4-7.

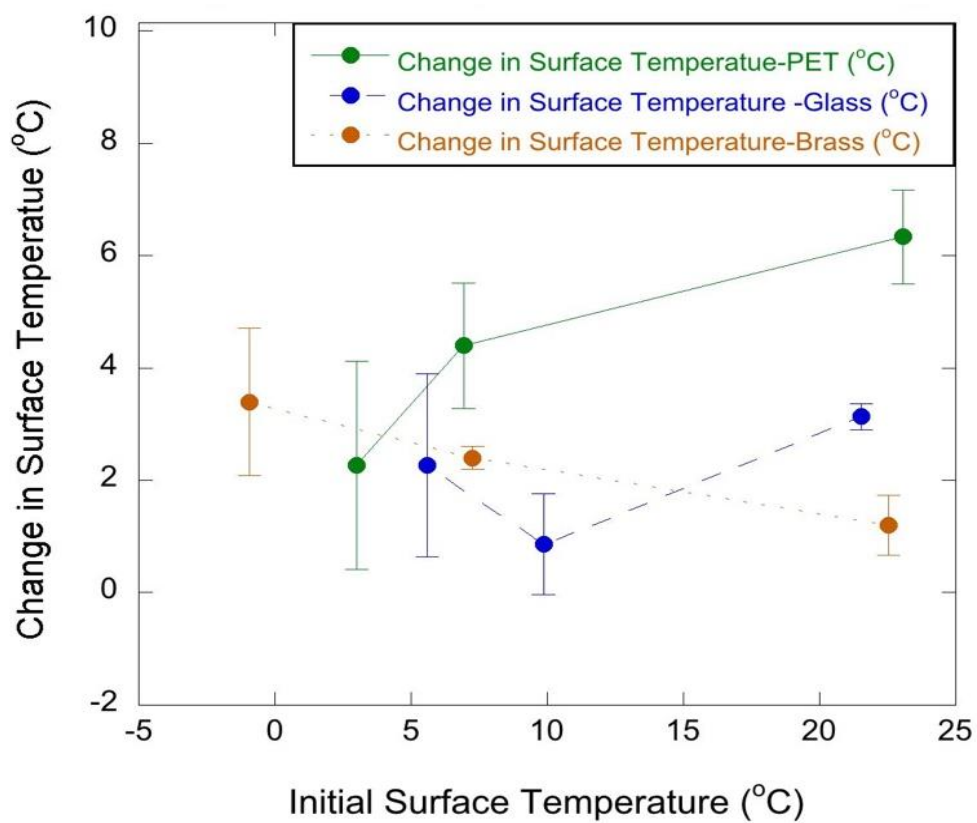


Figure 4-8: Change in surface temperature of each substrate during fumigating at ambient relative humidity

Average Number of PECA Chains

To ensure a holistic representation of the polymerization is provided for all surfaces, Figure 4-9 shows the measured average number of PECA chains on all surfaces. The average number of soluble chains (N_{ch}) was calculated using the following equation:

$$\text{Equation 1:} \quad N_{ch} = \frac{mass \times N_A}{M_n},$$

where mass is the average mass of PECA formed, N_A is Avogadro's number (6.02211×10^{23} molecules) and M_n is the number average molecular weight (g/mol). M_n is obtained from the GPC data. All substrates show an increase and peak in the number of chains at the medium surface temperature (between 5 and 10 °C). This trend was observed in previous studies in our lab in which the coupling effects of surface temperature and relative humidity were monitored. Based on those studies, polymerization of ECA which took place near 10 °C experienced the benefits of decreased surface temperature (minimized side reactions and chain transfer) and humidity (acts as a solvent to loosen ion pairs). This same phenomenon is apparent in this current study and is consistent across all the surfaces tested. The increase in the number of chains also correlates with an increase in the mass of PECA on each surface as well. Inspection of this figure shows that the fuming process on brass creates fewer chains with higher molecular weight (Figure 4-3), which is consistent with more successful propagation and fewer termination and chain transfer reactions. Similarly, the fuming process on the PET creates more chains than on brass, but fewer chains than on glass. This suggests that the propagation

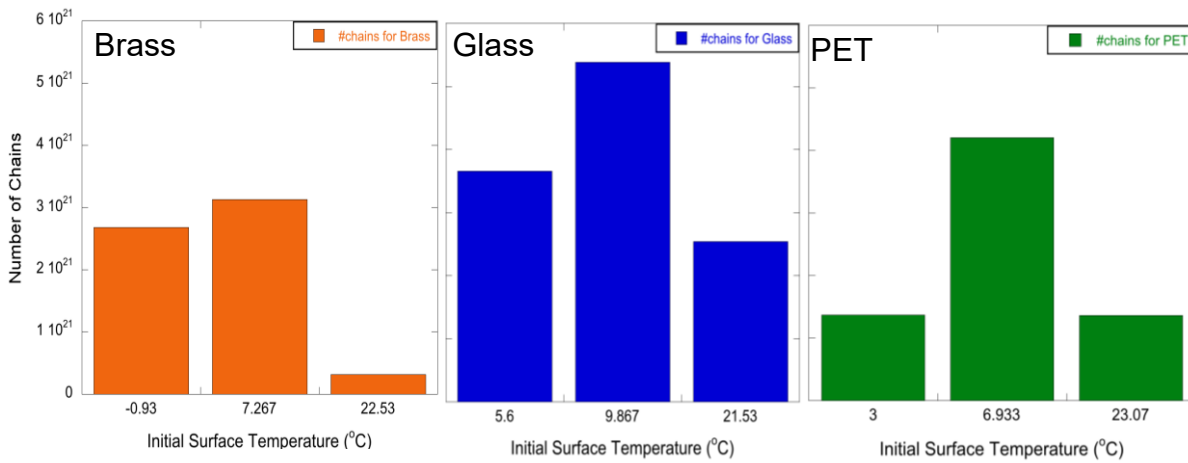


Figure 4-9: Average number of poly(ethyl cyanoacrylate) chains for brass, glass, and PET after fuming at surface temperatures ranging from -10 to 25 °C under ambient relative humidity.

reaction on PET is slower than on brass, but faster than on glass and/or there are more termination and chain transfer reactions on brass, but fewer of these reactions on glass.

These trends are consistent with the propensity of water to be present on the surface, i.e., the hydrophilicity of each surface. Glass has the lowest water contact angle and thus is most hydrophilic, while brass has the highest water contact angle and is the most hydrophobic (i.e., least hydrophilic). The PET has a water contact angle between that of brass and glass. Thus, one would expect that the glass surface to contain the most absorbed water, followed by PET, with very little adsorbed water on the brass surface. Given the complex role of water in the polymerization of ECA during fuming (potential initiator, ion solvent, and terminating/chain transfer agent), this propensity to allow or inhibit the adsorption of water on the surface appears to be a dominant mechanism in defining the role of a surface in the success of the fuming of latent prints by cyanoacrylate vapors.

Discussion

The results describe the role of surface functionality, hydrophobicity, and thermal conductivity on the amount of print residue that is deposited on the surface, as well as the success of the polymerization process during cyanoacrylate fuming. The thermal conductivity of the material does not appear to be a crucial parameter as the variation in temperature between surfaces is not significant. The hydrophilicity of the surface does

appear to be a crucial parameter that controls the success of the polymerization of ECA that occurs during fuming.

Our interpretation of this observation is that this response is connected to the complex role of water on the polymerization of ECA during the fuming of latent prints. It is known that water can serve as a terminating or chain transfer agent in anionic polymerizations. However, because the ethyl cyanoacrylate monomer is so reactive due to its electron withdrawing groups, water is also known to serve as a potential initiator of cyanoacrylates. At the same time, water solvates salts (such as sodium lactate) that are present in latent prints that can also serve as initiators in the polymerization of ECA during fuming.

Studies in our group, such as those described in Chapter 2, have observed that the adsorption of water on the surface on which a print resides tends to act as a terminating and/or chain transfer agent, decreasing amount of polymer formed, the number of polymer chains formed, and the molecular weight of the polymers formed. Examination of Figures 7 and 9 show that the brass surface creates the most polymer, but the fewest polymer chains. This suggests the polymerization on the brass surface is not limited by the presence of water, which correlates well to the fact that this surface is hydrophobic (water contact angle $\sim 94^\circ$). Conversely, the fuming of the print on the glass surface creates the least amount of polymer (particularly at the lowest temperatures) and the most polymer chains. This is consistent with a polymerization that is impacted by water as a terminating agent, which correlates well to the fact that this surface is hydrophilic (water contact angle $\sim 18^\circ$). The amount of polymer and number of chains

formed on the poly(ethylene terephthalate) surface is between that of the brass and glass surface, as is the water contact angle.

Thus, this study indicates that the hydrophilicity/hydrophobicity of a surface plays a key role in impacting the success of polymerization of ethyl cyanoacrylate fumes from a latent print. The hydrophobicity controls the amount of water than is found on the surface during the fuming process, which in turn impacts the polymerization reaction. A secondary effect found is that the composition of the surface impacts the amount of print residue. However, this is clearly an ancillary effect as the brass surface retains the least print residue, but fuming creates the most PECA on the brass surface print, particularly at low temperatures.

Conclusion

This study seeks to understand the impact of the structure and composition of the surface that a print resides on in the polymerization of ethyl cyanoacrylate during the fuming of latent fingerprints. These results show that on all surfaces studied (brass, glass, and PET) larger amounts of PECA were formed when the surface temperature of the surface is lowered to around 10 °C. These results, just as previous chapters, continue to highlight the importance of surface temperature and water in the polymerization of ECA. PET and glass produce comparable amounts of PECA over a range of surface temperatures while brass grows about three to four times the amount of PECA on the surface as PET and glass. The impact of surface composition, surface wettability, and the

thermal behavior of each surface on the success of the polymerization reactions were studied. The change in surface temperature for each surface coincided with reported thermal conductivities of the three surface materials. These result, however, do not indicate that the thermal conductivity is a primary determinant in the success of the polymerization reaction, as the change in surface temperature amongst the surfaces was minimal.

The water contact angle showed that glass is the most hydrophilic of the three surfaces, while brass is the most hydrophobic. Thus, the interaction of the surface with water may provide insight into the impact of the surface on the success of the polymerization reaction. It is well understood that water plays a vital role in the anionic polymerization of cyanoacrylates. Water acts as a solvent to loosen ion pairs on the growing polymer chain end, but may also terminate a generic anionic polymerization. Water can also act as a weak base initiator to polymerize ECA. Glass and PET are the more hydrophilic surfaces and are more prone to tolerate adsorbed water on their surfaces, which may interrupt the propagation reaction of the ECA polymerization. This leads to less PECA formed on the surfaces with lower molecular weight polymer, as was shown in our results. Because brass is hydrophobic in nature, it does not tolerate water as well, and thus there are fewer components that can interrupt the ECA polymerization, resulting in the growth of more high molecular weight PECA. The hydrophilic or hydrophobic nature of the surfaces therefore appears to be the dominant factor in determining the success of the polymerization of ECA on different surfaces.

CHAPTER 5 : CONCLUSION AND FUTURE WORK

Conclusions

Surface Temperature and Relative Humidity Studies

There is a competition of effects between surface temperature and relative humidity which affects the overall efficiency of the cyanoacrylate fuming method. Lowering the surface temperature during the cyanoacrylate fuming process loosens the ion pair at the growing end of a polymer chain and minimizes side reactions of the anionic polymerization, leading to increased propagation rate and higher molecular polymer. The prints with the highest amount of poly(ethyl cyanoacrylate) (PECA) on the surface and the higher molecular weight PECA were observed under ambient relative humidity with lower surface temperatures between 5-10 °C. Increasing the relative humidity led to more PECA on the substrate but a higher prevalence in overdevelopment and lower molecular weight PECA. Molecularly, increasing the moisture in the environment of the anionic polymerization solvates (or loosens) the ion pairs at the growing end of the PECA chain, leading to a higher reactivity for polymerization. The higher relative humidities exposed the anionic polymerization of the CFM to more water, which can also interrupt the chain growth process, producing lower molecular weight PECA.

In addition to lower molecular weight, visual analysis showed overdevelopment and lack of contrast between the deposited print and the surface

upon which it resided at the lowest temperature. Altering the length of fuming was beneficial in gaining insight to minimize the occurrence of background polymerization for ambient and 50% relative humidity. Altering the fuming temperature was less advantageous in minimizing overdevelopment at 80% relative humidity. As a result, lowering the surface temperature at high humidity provides little advantage in terms of the visualization of the print.

Overall, this work gives insight into the molecular processes governing the CFM and how changes in temperature, relative humidity, and time affect the final polymer on the print. It also demonstrates how controlling the relative humidity, length of fuming time, and the surface temperature of the print allows members of the forensic community to tailor the fuming process to their specific needs and how to minimize unfavorable results.

ECA Formulation Studies

Lumicyano is a cyanoacrylate formulation growing in popularity due to its one-step fuming protocol which circumvents the need for post-treatment of developed prints due to the colored, fluorescent poly(ethyl cyanoacrylate) on the surface of the print enhancing background contrast. 3-chloro-6-ethoxy 1,2,4,5-tetrazine is the compound responsible for the vibrant hue of the PECA. In order to identify if and how the incorporation of this tetrazine component affects the

polymerization process and resulting PECA chains, the cyanoacrylate fuming method was conducted on Lumicyano and Sirchie OMEGA-Print, “unmodified ECA”, with varying protocols over a range of surface temperatures for comparison. Fuming time and monomer vaporization studies were also conducted to gain a more holistic understanding of the behavior of Lumicyano during fuming.

Both formulations developed the print to similar visual contrast, except the Lumicyano has a vibrant color which made observation of print detail easier. This contrast was further enhanced when observed under fluorescent light. Fuming with Sirchie and Lumicyano resulted in background polymerization and overdevelopment of prints below 10 °C, surface temperatures at which condensation of water on the surface is common. Our studies revealed Lumicyano vaporizes more slowly than Sirchie OMEGA-Print yet consistently produces similar mass and molecular weight PECA as Sirchie. For Lumicyano, the longer fuming time results in more, longer chain (higher molecular weight) PECA while there was little advantage or change in the PECA that is formed if the Sirchie OMEGA-Print is fumed for a longer time. It appears that the propagation of the pECA polymerization during cyanoacrylate fuming with Lumicyano proceeds more steadily due to the presence of the 3-choro-6-ethoxy 1,2,4,5-tetrazine. A potential explanation for this behavior is that the tetrazine loosely coordinates with the ion pair at the end of the growing polymer chain, protecting the chain end from side reactions that can cause chain transfer and termination. Therefore, the presence

of tetrazine in the Lumicyano formulation couples with the ions at the end of the growing PECA chain to enable a slower, yet steady propagation via the protection from side reactions. Overall, Lumicyano is an excellent one-step alternative to unmodified ECA formulations in that it enhances visualization of developed prints and attains similar quantities of PECA with higher molecular weight and fewer polymer chains.

Surface Studies

By performing the CFM on glass, poly(ethylene terephthalate), and brass we gained insight into the role a surface plays in the polymerization of ethyl cyanoacrylate during fuming. Each surface selected represents a frequently encountered substrate at a crime scene. Based on our results, all surfaces had larger amounts of PECA when the surface temperature was lowered to between 5 and 10 °C. As shown in our previous results, the lower surface temperature aids the anionic polymerization by loosening ion pairs at the reacting end of a polymer chain and minimizing side reactions; therefore, decreasing chain transfer. In these studies, the prints that are fumed on the PET and glass produce comparable amounts of PECA over a range of surface temperatures while brass grows about three to four times the amount of PECA on the surface as PET and glass.

The molecular weight of PECA on brass and glass steadily increased as surface temperature increased but the opposite trend was observed with PET. Surface composition, surface wettability, and the thermal behavior of each surface were studied. The change in surface temperature for each surface coincided with reported thermal conductivities in that brass showed the least change in surface temperature, consistent with it having the highest thermal conductivity of the three surfaces. PET possesses the lowest thermal conductivity, retaining the heat and having the greatest increase in surface temperature change during fuming. This data, however, does not indicate that the thermal conductivity of the surfaces controls the polymerization process, as the change in surface temperature amongst the surfaces was minimal.

The water contact angle showed that glass has the lowest contact angle, therefore is the most hydrophilic and brass had the highest water contact angle, therefore is the most hydrophobic. It is well known that water, whether in the air as humidity or on the surface when condensed, plays a vital role in anionic polymerization. Water acts as a solvent to loosen ion pairs in the chain propagation but may also serves as a chain transfer agent and terminator in anionic polymerizations. Water can also act as a weak base initiator to polymerize ECA. Glass and PET are hydrophilic surfaces and are therefore more prone to collect and absorb water on their surfaces, enabling termination or side reactions. This leads to less PECA on the surfaces with lower molecular weight polymer, as

shown in our results. Because brass is hydrophobic in nature, there is little water adsorption on the surface, which permits more, high molecular weight PECA to grow. The hydrophilic or hydrophobic nature of the surfaces therefore, appear to be the dominant factor in determining the impact of the surface on the polymerization of ECA.

Collectively, this research offers fundamental insight to the forensic community as it provides insight into the molecular level processes that govern the fuming process of latent prints as a result of variations in surface temperature, relative humidity, fuming time, ECA formulation, and surface identity. The data obtained provides an understanding of variables which can guide crime scene investigators to tailor the cyanoacrylate fuming method to bias the fingerprint visualization towards success and provides scientists with more understanding of factors affecting the molecular behavior of this anionic polymerization, despite having little control of the environment in which the polymerization is carried out.

Future Work

Surface Temperature and Relative Humidity

All of the reported data in this study focused on surface temperature at room temperature or below. The benefits of lower surface temperature were only

observed for ambient relative humidity as 50 and 80 percent relative humidity experienced copious amounts of condensation on the surface and overdevelopment of the prints. Decreasing the fuming time also did not provide a great advantage in the fuming process for higher humidity due to the lack of detail and contrast between the deposited print and the glass surface. In order to identify an ideal surface temperature for higher humidities, the surface temperature range can be shifted to include surface temperatures from 5 °C to 60 °C. The largest amount of PECA on the surface was observed near 5 °C for 50% relative humidity and between 5 and 15 °C for 80% relative humidity. The largest amount of PECA for both relative humidities was comparable to the largest observed for ambient relative humidity studies. The study should continue to focus on maximizing the visual contrast of the print from the background paired with large amounts of higher molecular weight PECA on the surface.

The reported data for these studies were performed utilizing a copper block attached to an isotherm with prints on glass stored in a drawer. Our results show fuming with a lower surface temperature is beneficial. Previous research by Steele et al have shown storing surfaces for CFM in a refrigerator until it reaches what was found to be an ideal temperature before conducting the CFM produced enhanced visualization of fingerprints. Our work can be furthered by examining the impact of storing the prints in the refrigerator for at least 12 -24 hours prior to deposition with the refrigerator set to 32 °F (0 °C) up to 50 °F (10 °C) which is the

range where the largest amount of PECA was present on the surface at ambient relative humidity. This would give insight into whether pre-cooling, such as done by Steele et al., for an extended time would enhance the overall polymeric properties and provide a protocol that is more easily implemented in a forensic lab.

ECA formulation

As a next step, studies into whether double fuming, such as conducted by Farrugia et al, at lower surface temperatures would affect the final polymeric properties of “un-modified” ECA could be conducted.⁷⁷ Our results indicate Sirchie OMEGA-Print does not benefit from a longer fuming time. The main objective would be to determine if an “un-modified” ECA formulation, such as Sirchie-OMEGA Print, could benefit from an additional round of cyanoacrylate fuming. The focus would be to determine if an additional fuming treatment introduces a higher prevalence of background fuming and if the newly vaporized ECA prefers the PECA on the fingerprints over the substrate which would lead to the enhancement of the previously visualized fingerprints.

For our formulation studies, the Lumicyano fuming was conducted under the manufacturer’s protocol and our standard and revised CFM protocols. In order to give a more complete assessment of the performance of both formulations, completing the cyanoacrylate fuming method with the Sirchie OMEGA-Print with

the hot plate temperature increasing to 120 °C over 10 minutes and being held at that temperature for another ten minutes should be considered. The minimum fuming temperature for unmodified ECA to sufficiently fume is 120 °C. Observing the fumed prints at the ten-minute mark as well as after twenty minutes will provide further insight into the impact of lower fuming temperature on the molecular properties of the formed PECA at ambient, 50, and 80% relative humidity. The lower fuming temperature could decrease the condensation on the surface as well as minimize background polymerization. Overall, when combined with the results from our current studies, these studies could identify which formulation gives the best print development as well as how the polymerizations are proceeding regardless of any alterations in the fuming protocol.

Surfaces

Stainless steel is considered one of the most challenging surfaces to visualize latent fingerprints for any enhancement method due to its limited thermal conductivity as well as its semi-porous chromium oxide layer. This oxide layer alters the surface chemistry and interactions at the surface with its surroundings, and impacts the diffusion of the fingerprint on the surface.⁶⁴ Previous studies have examined the CFM process on prints that reside on stainless steel at 80% relative humidity and using Cyanobloom and Lumicyano cyanoacrylate formulations.³¹

The results showed migration of the fingerprint components around the surface before development took place, where it was postulated that the present moisture enabled the fingerprint constituents to diffuse. Based on our results, the tendency of a surface to absorb water dominates the progression of ECA polymerization on the surface during fuming. Stainless steel is hydrophilic with a reported contact angle of 49.5° , below the measured contact angle of PET but above that measured for glass in our studies. Further examination of the success of the fuming process on stainless steel using the protocols described in the thesis may provide the foundation to fine-tune the surface temperature and relative humidity to effectively visualize fingerprints on stainless steel by the cyanoacrylate fuming method.

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VITA

Leondra Lawson-Johnson was born in Jackson, MS. Leondra obtained her Bachelor of Science degree in chemistry with a concentration in forensic chemistry from Jackson State University. She became a fellow in the Louis Stokes Mississippi Alliance for Minority Participation at Jackson State University and obtained a Master of Science in environmental chemistry. This work led to her first published work in a scientific journal. Subsequently, she joined Dr. Mark Dadmun's research group in the department of chemistry at the University of Tennessee, Knoxville where she returned to her love for forensic chemistry. While at the University of Tennessee, Knoxville, Leondra became a fellow in the Program for Excellence and Equity in Research program. She has shared her love for science and forensics through presentations to a diverse group of local middle and high school students. She has obtained a Master of Science degree in Polymer Chemistry and will continue to encourage youth to pursue careers in STEM (science, technology, engineering, and mathematics) fields.