Article

Forced Condensation of Cyanoacrylate with Temperature Control of the Evidence Surface to Modify Polymer Formation and Improve Fingerprint Visualization

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Abstract: Tests involving temperature control of both the cyanoacrylate fuming environment and the evidence surface performed at Mountain State University Forensics Program, Beckley, West Virginia, have identified conditions to improve the visualization of fingerprints. Proper temperature controls resulted in increased cyanoacrylate deposition, modification of the pseudo-crystalline structure, and increased contrast. This research program has identified a controlled micro-crystalline structure modification of the polymer formation specific to latent fingerprints. The poly-ethylcyanoacrylate polymer structure can be controlled to yield a much more visible form due to the crystalline structure under these temperature controlled environments. This research also empirically suggests that the forced condensation of the cyanoacrylate deposition follows a specific heat capacity linear curve based on the evidence material type. Different material types have demonstrated this phenomenon in controlled temperature tests and we forecast that the polymer deposition could be forced to behave in certain ways based on the type of evidence material with temperature control of the evidence surface.

The use of these forced condensation techniques via temperature control add visual detection sensitivity to evidence processing protocols.

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Introduction

Under ambient processing conditions, ethylcyanoacrylate is heated to a vapor that will react with biological residue (forming a fingerprint), condensing and polymerizing into poly-ethylcyanoacrylate (Figure 1).

When viewed microscopically, the physical form of the poly-ethylcyanoacrylate formed in this process is globular, curing into a translucent to transparent state that can be visualized and recorded by several means that are well documented in the literature.

Regardless of the test methods employed, the visualization of poly-ethylcyanoacrylate fingerprints is dependent on color, reflection, and refraction.

As light passes from one transparent media to another, such as from air to plastic, it will bend relative to the refractive indices of the two materials and the wavelength of the incident light [1] (Figure 2). This is critical in understanding the optical properties of polymers because the solids are a series of polymer chains overlapping each other around interstices of air. So light passing through a polymer makes many transitions from air to resin and back again. When transparent polymers cure or solidify into a highly ordered structure (e.g., drawn fibers or films), the uniform orientation of these layers results in a net cancellation where light is bent and bent back essentially to its starting angle, creating a highly transparent solid.

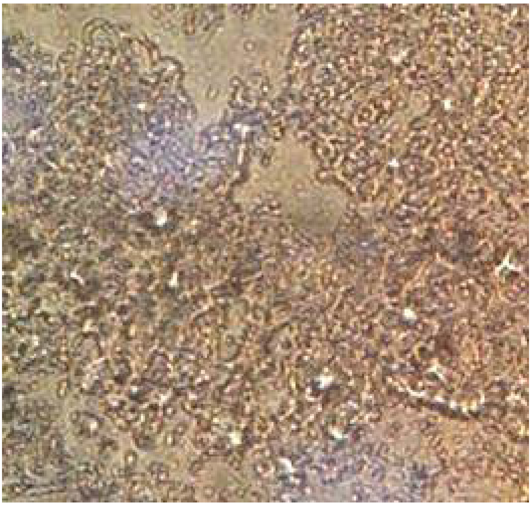

Figure 1

Poly-ethylcyanoacrylate.

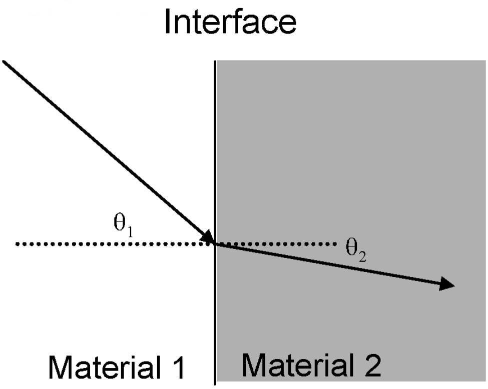

Figure 2

Light bends when passing from one media to a different media (θ indicates the angle relative to the surface).

However, under different processing conditions, such as rapid cooling, even normally transparent resins can take on a random lattice structure where the interfaces are at angles to each other (Figure 3). In such cases, the plastic becomes more opaque as light is refracted randomly, resulting in a variety of optical interference phenomena. Strobl [2] describes the process by which a polymer forms both crystalline and disorganized areas when rapidly cooled below the polymer's melting point. When the cyanoacrylate vapor comes into contact with the cooled evidence, the temperature of the vapor rapidly drops and a semi-crystalline state is formed. Obviously, factors that affect the rate of cooling (e.g., the temperature of the evidence relative to the melting point of the poly-ethylcyanoacrylate, the heat conductivity of the evidence, and the specific heat capacity of the print and evidence) should impact this process.

This is important because when light strikes a reflective surface, it bounces off at the opposite angle. When the surface is irregular, the light striking the surface is reflected in many different directions (Figure 4).

The irregularity of the surface can also impact the ability to induce color through the application of dyes or coatings. Once the poly-ethylcyanoacrylate has cured into the shape of the fingerprint, many protocols call for coloration. Regardless of whether the coloration method is a dye stain or a pigment coating, the amount of color deposited on the fingerprint is related to the total surface area.

Because of the effects of temperature, poly-ethylcyanoacrylate crystal deposition during cyanoacrylate fuming can generally occur in two basic configurations (Figure 5). The smooth, globular formation (Figure 5, left side) generally occurs at the higher evidence surface temperature. The globular formation appears to be similar in structure to droplets of liquid with rounded formations that do not reflect light very well, and in some instances, have little receptivity to dye staining techniques. The more active steel wool type formation (Figure 5, right side) generally occurs at the lower evidence surface temperature. The crystal formation is radically striated with much more surface area at the microscopic level when the evidence temperature is cooled relative to its specific heat capacity.

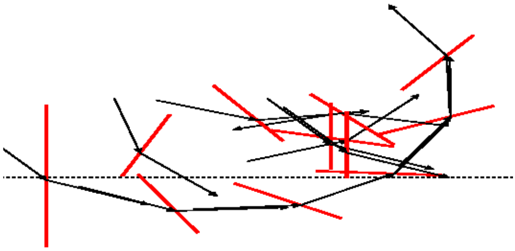

Figure 3

The internal structure of polymers can be seen as a semi-random collection of surfaces at inconsistent angels relative to each other. As light passes through these surfaces, it bends and is scattered in many directions.

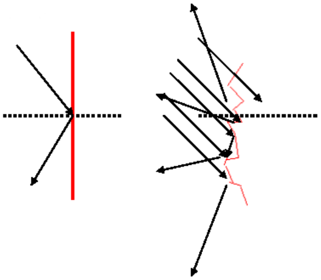

Figure 4

When light reflects off an irregular surface, the reflection will be scattered.

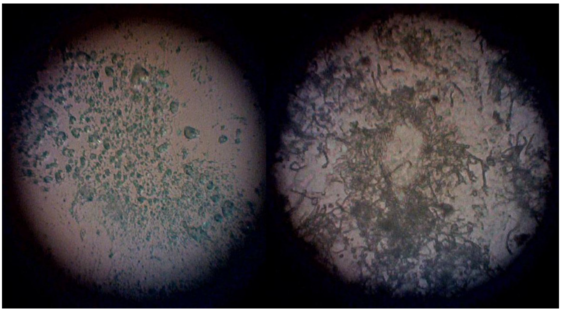

Figure 5

Image on the left is a 250X magnification of a latent print on glass held at 72 °F prior to cyanoacrylate fuming. Image on the right is a 250X magnification of a latent print on glass cooled to 46 °F prior to cyanoacrylate fuming. These samples were simultaneously processed. Images were obtained using transmitted lighting.

The surface area of the polymer on the left reflects and absorbs light in a radically different way than the polymer on the right. Highly irregular surfaces typically have more surface area than smooth surfaces, thus providing more area for traditional dye staining absorption such as rhodamine 6-G and other secondary dye staining applications. Highly irregular surfaces have more surface area than smooth surfaces. As a result, highly irregular surfaces have more opportunity for color uptake.

In addition, previous experiments found that several materials showed an increased deposition on the fingerprint of greater than 0.001g more poly-ethylcyanoacrylate when the samples were cooled relative to the ambient chamber temperature [3].

Figure 6 shows three test tubes. The top test tube was processed at 46 °F, the middle test tube at 65 °F, and the bottom test tube at 74 °F. Images were obtained using oblique lighting. All three test tubes were simultaneously processed in the same chamber. The only difference was the test tubes' surface temperature.

The greatest increase in poly-ethylcyanoacrylate deposition was noticed when the sample temperature was 5 °F to 20 °F cooler than the ambient chamber environment (typically 72 °F to 80 °F). Samples less than 5 °F cooler than the ambient showed no measurable difference with ambient samples. Temperature differences in excess of 20 °F cooler showed no further improvement. However, the greatest visual impact was seen at specific temperatures for each material (Table 1).

Material	Specific Heat Capacity	Processing Temp
Aluminum	.91	69 °F
Copper	.39	71 °F
Glass	.84	46 °F
Polyethylene	.54	51 °F
Steel	.44-.49	65 °F

Table 1

The specific heat capacity of target materials and the ideal evidence temperature relative to an 80 °F chamber.

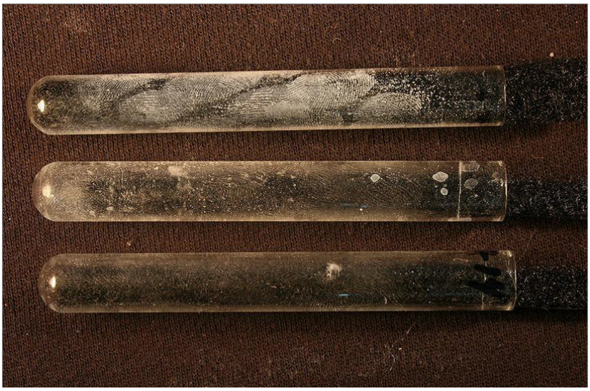

Figure 6

Glass tubes at three temperatures.

Experiments

These experiments focused on changing the deposition of poly-ethylcyanoacrylate by varying the temperature of the evidence relative to the ambient temperature of the air within the enclosed chamber environment.

Materials and Methods

In order to determine how the substrate temperature of various substrate types affects the development of latent fingerprints developed with cyanoacrylate, three substrate types were tested (glass, copper, zinc–steel alloy) at various temperatures. For the glass tests, fingerprints were deposited on Pyrex test tubes and pieces of plate glass that could be weighed before and after fuming to determine the amount of poly-ethylcyanoacrylate deposited. The copper samples were cut from thin copper sheeting used for decorative banding (K&S Engineering #6540). The steel samples were common steel–zinc washers (Fender #290042).

Simultaneous cyanoacrylate fuming events were run, exposing identical materials to the same volume of fumes in a controlled environment. The material temperatures and the chamber temperature and humidity were carefully monitored with a digital, infrared thermometer and a digital hygrometer.

One hundred pieces of each material type were numbered then carefully weighed three times each on a scientific, digital scale, and the weights were noted. A subject was then selected to leave fingerprints and palmprints. The subject's fingers and hands were oiled by rubbing on his forehead prior to print deposition. Then his fingerprints or palmprints were deposited on each side of the material's surface using medium pressure.

The items were then grouped in sets of 25; one-half were refrigerated and one-half were stored at room temperature. When the refrigerated group reached what we earlier determined as the optimum temperature (46 °F for glass, 71 °F for copper, and 65 °F for the steel–zinc washers), one group of 25 items was removed from the refrigerator and quickly placed into the monitored fuming chamber with the 25 identical items that had been held at room temperature. Fuming then began immediately. The amount of cyanoacrylate was premeasured and the entire fuming event was timed. After the cyanoacrylate was vaporized, the material was left in the chamber for 10 minutes to allow complete polymerization to occur.

After the fuming event, the materials were carefully removed from the chamber and examined visually to note any difference in appearance. The materials were again carefully weighed three times and the weights were noted for statistical evaluation. Consistently, the phenomenon showed itself to be temperature sensitive, and the opacity of the cooled samples was visually greater. The potential for improved dye staining or other preferential adherence and mechanical functions by utilizing this cooling technique therefore seemed promising.

To test the impact on dye staining, fingerprints on glass were evolved at two temperatures. Sample set 1 was prepared by cooling the sample to 46 °F before fuming at 75 °F. Sample set 2 was prepared by cooling to 72 °F before fuming at 75 °F. Each set consisted of 10 pieces of fingerprinted optical glass. As can be seen in Figure 7, as mentioned, the overall structure of the cooled sample is smaller globs, yielding more surface area. Therefore, it is expected that availability for dye uptake is greater.

Both sample sets were then stained with rhodamine 6G according to the method outlined in the FBI Processing Guide for Developing Latent Prints [4] except that no M.B.D. was used. The samples were stained by dipping simultaneously for five seconds in the dye. Upon visual examination, the cooled samples did appear to have significantly more dye adherence and fluoresced more strongly (Figure 8).

Figure 7

Shown here are examples of poly-ethylcyanoacrylate at 400 X. When the sample is cooled prior to fuming (right side), the sample yield is smaller globs than when processed at room temperature (left side), yielding more surface area. Therefore, it is expected that availability for dye uptake is greater.

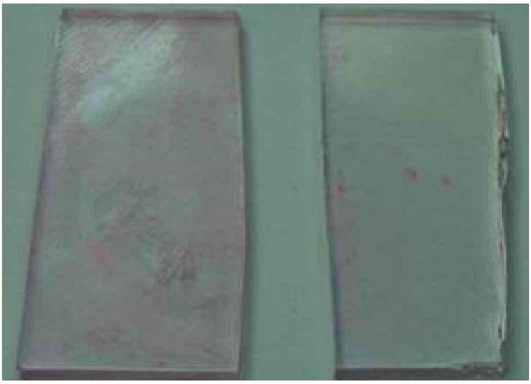

Figure 8

Cooled (left side) versus uncooled (right side) samples after dyeing.

For a quantitative measure, the samples were placed in a Turner Fluorometer selected for reflection. Because rhodamine 6G has a strong emission from 520 nm to 650 nm (Figure 9), the total energy on the detector in this range was collected for each sample when the sample excited. On average, the cooled samples exhibited a fluorescence emission increase of three to five times the uncooled sample (meter readings of 10 to 15V versus 2 to 5V).

The samples were then scanned for absorption with a Cary 200 UV-Vis spectrophotometer to determine the actual dye concentration relative to poly-ethylcyanoacrylate deposition. Rhodamine 6G has a strong absorption between 520 nm and 580 nm, peaking near 560 nm (Figure 10).

Poly-ethylcyanoacrylate has no appreciable peak at this location and different UV spectra above 340 nm. It is therefore possible to quantify the absorption of both components separately via the Beers-Lambert equation.

Using these data, the relative dye concentration per poly-ethylcyanoacrylate, the cooled samples accepted 2.33 times the dye of the uncooled samples[1].

The apparent variation between the increases in fluorescent strength versus the actual increase in dye concentration is easily understood if we look again at the internal randomness caused by the cooling of the sample.

Poly-ethylcyanoacrylate is a normally clear polymer. As a result, more than half of the fluorescence transmits through the sample, either to be lost or reflected. The greater opacity caused by the cooling allows more of the fluorescent emission to be reflected from the layers near the surface of the sample.

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[1] A concentration curve of each was not run to put these data into ppm.

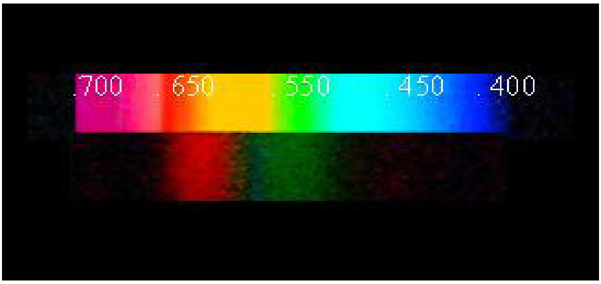

Figure 9
Emission of rhodamine 6G.

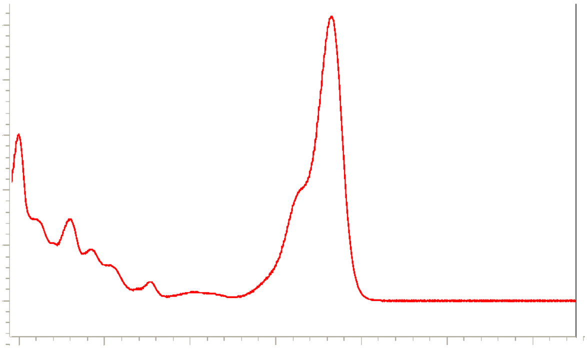

Figure 10
Absorption of rhodamine 6G.

Results and Discussion

The mass of poly-ethylcyanoacrylate deposited when the samples were cooled was often significantly greater than samples processed at room temperature. It should be noted that the primary weakness of the data collected relative to mass was that the variability of equipment was in the same order of magnitude as the values being measured. As a result, although fingerprints were observed on all samples, the actual mass of cyanoacylate deposited was only measureable in about 75% of the cases for both the cooled and room temperature samples. The resulting effect was that any statistical analysis produced a lower than desirable confidence level and further research is being conducted to improve the resolution of these data. However, we can state that the resulting mass of deposition was at least equal to room temperate processing and offered the potential to improve the resolution of lighter prints.

Regardless of the mass of the deposited poly-ethylcyanoacrylate, visibility was increased in virtually all cases. Two possible explanations for the change in physical form are change in polymerization because of rapid cooling and some unexplained chemical change. Samples of each temperature variant were scanned from 190 nm to 800 nm on a Varian DMS 200. Neither sample had any unique peaks that would have indicated a chemical change. But, the cooled sample had substantially more noise in the scan.

The most likely reason for the increase in visibility therefore is the opacity resulting from optical interference caused by the more randomized pseudo-crystalline structure. When the samples were measured according to their relative turbidity, we found that the turbidity of the cooled sample was 50.2 NTU; the ambient sample was 25.4 NTU.

This visible difference between the cooled and room temperature samples was microscopically detectable. The cooled samples polymerized into substantially smaller globs than did ambient temperature samples, which were visible under magnification (Figure 7). In addition, many long, fiberlike strands were seen, indicating that there were many more discrete sites initiating polymerization. These fiber strands wove together randomly, and the smaller particles created a substantial increase in surface area. Assuming that these microscopic geometries are indicative of the pseudo-crystalline habit of the polymer, the increase in opacity seems directly related to the rate of cooling.

Proper cooling of a sample relative to the environment resulted in several changes that increased visualization:

- First, decreasing the temperature 5 °F to 20 °F relative to the ambient environment potentially caused more cyanoacrylate to condense on the fingerprint, allowing for greater resolution.
- Second, it changed the physical form of the poly-ethylcyanoacrylate product, making the print more opaque, improving contrast.
- Third, the resulting poly-ethylcyanoacrylate had substantially more surface area, which provided for more opportunity for color uptake.

Conclusion

The results of the research into this phenomenon indicate a significant increase in detection sensitivity for cyanoacrylate-developed latent fingerprints by simply manipulating the evidence temperature during the fuming event. A pre-cooling of the nonporous evidence of 5 °F to 20°F prior to chamber fuming appears to consistently yield higher resolution fingerprint development as evidenced in more than 1,000 pieces of material processed. The visualization of poly-ethylcyanoacrylate fingerprints, which is dependent on color, reflection, and refraction, can be measurably improved when the nonporous evidence is refrigerated immediately prior to processing. There also appears to be a significant increase of adherence during secondary treatments, such as rhodamine 6-G dye staining, of latents processed at these cooler temperatures. Future evidence processing environments will most likely include temperature and relative humidity controls for chamber processing events. The research continues at Mountain State University, and the Sirchie Fingerprint Laboratories Inc. of North Carolina has signed on as a strategic partner in this research, currently designing and constructing a self-contained, commercial-grade “environmental chamber”, which will provide both a refrigeration chamber to cool the evidence and a humidity controlled chamber for the actual fuming of the evidence.

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