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The reconstruction of serial numbers in polymers: recent progress, challenges and perspectives

Article Category: Overview

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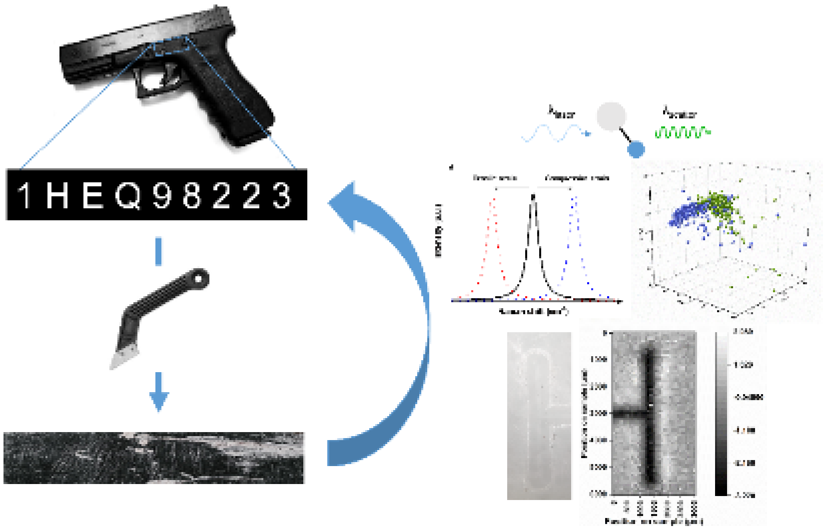
ABSTRACT

The mass production of polymers has forced forensic practitioners to reconsider traditional methods of traces analysis. The field of impression reconstruction, specifically markings in firearms, is a prime example. This overview offers a critical evaluation of the relevant published techniques for the reconstruction of serial number in polymers, which include destructive methods such as swelling, heat treatments and relief polishing as well as methods allowing for trace preservation, such as hyperspectral Raman imaging combined with multivariate statistical analysis for enhanced pertinent data extraction. It therefore provides a complementary compilation to existing protocols for metal substrates.

The novelty of this work lies within its approach, specifically by establishing not only the mechanistic scientific explanation for suitable comprehension and application of the techniques, but also by properly assessing their relevance considering the use in a forensic science context.

The potential of wide-field imaging techniques, mainly auto-fluorescence analysis, is suggested for faster acquisition and reduced data processing (i.e. decreased time and greater accessibility). Additionally, application of the acquired knowledge to other relevant forensic traces, such as failure analysis of 3D printed objects, is proposed. Emphasis is also placed on the relevance of a purposeful interpretative framework necessary to reconstruct the singular past of the obliterated serial number thus leading to the identification of the given object in which it is affixed.

GRAPHICAL ABSTRACT



KEYWORDS

Firearms, Hyperspectral imaging, Residual strain analysis, Data mining, Interpretative framework

1 INTRODUCTION

The serial number, usually a sequence of alphanumeric characters, introduced in firearms (as shown in figure 1), vehicle parts, orthopedic prosthesis and implanted medical devices for example, ensures a sure and secure level of traceability (i.e. chain of ''ownership'', association to previous locations) of the object in which it is affixed (Baiker-Sørensen et al., 2019; UNGA, 2014). Allowing for identification or individualisation of a given item, the sequential characters may provide investigative leads and become circumstantial evidence in a judicial trial. At the very least, the number aids in returning the object to the rightful owner.

Polymers are frequently used today for the fabrication of firearms. Their mass production (Paoli, 2015; UNGA, 2014), combined with criminal activity has created a significant need for the development of methods to reconstruct obliterated serial numbers in this specific type of material. As these kinds of weapons are generally easy to conceal in comparison to their metal counterparts, the increasing trend shows no signs of subsiding. Although not specific to polymeric firearms, the Johns Hopkins Center for Gun Policy and Research has stated that '' nationwide (USA) an estimated 9 to 20 percent of the recovered crime-guns had their serial numbers removed '' (ATF, 2001).

Introducing these characters, particularly by means of stamping, leads to elastic and plastic deformations (Katterwe, 2006; Parisien et al., 2017; Parisien et al., 2019), which propagate even deeper into the object than the initial relief and remain even when the latter is superficially damaged (i.e. defined in terms of visibility by the human eye). As the local deformation and structural distortion pattern extends over the same region as the initial impression, some techniques, such as chemical swelling, heat treatment, relief polishing (Katterwe, 1994, 2006) and Raman spectroscopy (Parisien et al., 2017; Parisien et al., 2019) have been reported as successful for the reconstruction of obliterated information. Regardless, comprehension of the deformation and reconstruction mechanisms in polymers is still rather fragmental due to, among other things, the complexity and multiplicity of polymeric structures.

Although previous reviews about the retrieval of serial numbers in polymeric structures have recently been published (Uysal et al., 2020), the fundamental understanding of the propagation and reconstruction mechanisms (at least from a material science point of view) are not fully addressed, nor is the assessment of the relevance and feasibility of the techniques in a forensic science context. This overview offers a comprehensive evaluation of scientific literature on the reconstruction of obliterated serial numbers in polymers. It specifically describes the pertinent scientific mechanisms, outlines the experimental methods, needs and limitations as well as highlights the importance of considering the intrinsic characteristics of the trace (i.e. the alphanumeric character). It also offers suitable experimental perspectives and a path to a necessary interpretative framework (i.e. logical reasoning). It is worth mentioning that this overview is complementary to the existing protocols for the reconstruction of serial numbers in metals.

2 SERIAL NUMBER REGULATIONS IN FIREARMS

Most developed countries provide legal framework for weapons marking and recording. In fact, the Firearms Protocol and the International Tracing Instrument (ITI), adopted by the United Nations, respectively in 2001 and 2005, constitute politically binding agreements defining marking requirements (UNGA, 2001, 2005).

In addition, knowingly tampering with the serial number (e.g. removing, altering, obliterating, defacing) is forbidden and can lead to legal ramifications in many countries.

The following section offers specifications (when available) in North America. It does not provide an exhaustive list of regulations, but a broad overview to provide references and pertinent framework for experimental relevance assessment.

North America

In the United States, section 923(i) of the Gun Control Act of 1968 (GCA), as amended (18 U.S.C. Chapter 44), requires licensed importers and manufacturers to identify each firearm by means of a serial number, which must be engraved, cast, or stamped on the receiver or frame of the weapon. These regulations specifically prescribe a minimum height or print size of 1/16 inch (≈ 1.588 mm) and a minimum depth of 0.003 inch (≈ 0.076 mm) for serial numbers (ATF, 2001).

In attempts to quell ghost gun proliferation, a new executive rule has been issued by the U.S. Department of Justice under the Biden administration, mandating manufacturers of gun kits (i.e. ‘buy build shoot’ kits) nationwide to issue weapons carrying serial numbers (House, 2022). This mandate therefore has the potential of increasing the number of serial number recovery cases in full or partial polymeric firearms.

Similarly, in Canada, the Firearms Marking Regulations (SOR/2004-275, coming into force on December 1st 2023), made under the Firearms Act, states that ‘’every individual or business that manufactures a firearm shall ensure that the firearm is marked, at the time of manufacture’’. This number ‘’ shall be marked by permanently stamping or engraving on the firearm’s frame or receiver’’ and ‘’have a depth of at least 0.076 mm and a height of at least 1.58 mm (Canada, 2009)’’.

These standards and regulations can help practitioners with identifying relevant areas for deformation propagation analysis. Information can also be obtained from the firearm manufacturer to assist in determining the location of the initial marking. In most cases, the obliteration area (i.e., the location of the serial number) will likely result in a roughened surface that can be easily detected by the forensic expert attempting to recover the content.

3 INTRODUCTION METHODS

Stamping methods (including press as well as roll markings), micropercussion (or dot peen) and mechanical grinding create physical indentations leading to plastic deformations (the extents of the latter vary from one technique to the other). As stamping has proven to be the more prevalent and reliable technique, most publications regarding the reconstruction of serial numbers in polymers have studied this type of introduction method (Katterwe, 1994, 2006; Paoli, 2010, 2013, 2015).

Chemical etching and engraving are also used for creating traceable information. These methods cause parts of the material to be removed by acids leading to superficial cavities. However, it has been noted that the experimental conditions are harder to control and can jeopardize the polymeric structure. Other methods are therefore privileged for firearm markings as these objects undergo relatively high temperatures and pressures at shooting (Paoli, 2010, 2015).

Marks can also be incorporated into the firearm by laser annealing (i.e. densification and compaction of the surface), oxidisation (i.e. colour change) or ablation (i.e. surface depletion by vaporisation or sublimation). These techniques are mainly distinguished by the selected laser intensity. Some scholars have suggested possible recovery of laser induced markings in polymeric materials (Katterwe, 1994), following the scanning electron microscope (SEM) analysis of a heat-affected zone, though it has not been fully investigated. Evaluation of the propagation and extent of the laser effects which depend among other things on the ablation threshold as well as the absorption coefficient and thermal conductivity of the polymer in question should therefore be performed (Ravi-Kumar et al., 2019).

Indirect markings, for instance metal tags embedded in the polymeric frame, are also a possible introduction technique (Paoli, 2015). As these are generally easy to remove and do not generate elastic or plastic deformations in the firearms, other methods are favoured for traceability purposes.

FIGURE 1 A Smith & Wesson M&P 40 polymer air pistol with its serial number (framed in blue). The frame of the weapon is made of Zytel^{TM} (Dupont^{TM}), a thermoplastic of the polyamide family. Figure courtesy of Cédric Parisien.

Deformation and propagation mechanisms in polymers – Residual strain

Although an accurate comprehension of theoretical concepts for proper assessment of reconstruction techniques is required, the interpretation of deformation mechanisms in polymers presents some ambiguities as a result of the complex and diverse nature of structures (Askeland et al., 2011).

The presence of stress, e.g., due to the application of an external force, results in the modification and distortion of the chains and cross-links (if any) of the polymer, which may subsequently be manifested as residual strain (as depicted in figure 2). This distortion can act on the backbone or on the monomeric components of the polymer. In the particular case of thermoplastics, such as polyethylene, polycarbonate and nylon, it is generally the Van-der-Waals bonds between the molecules constituting the polymer chains that weaken first under the application of an external force exceeding the elastic limit (Askeland et al., 2011). Indeed, it is more likely that mechanical stress will first change the distance between polymer chains (non-universally detecting changes on a certain length scale) before affecting the monomeric structure (i.e. would require higher forces).

The way this distortion is introduced depends, among other things, on the orientation of the polymer with respect to the deforming stress (Flory & Rehner, 1943). However, it is possible to generally state that during deformation, the polymer undergoes an alignment of certain chains in the direction of the applied stress. This consequently generates a preferential orientation and reinforces structural heterogeneities (anisotropy in some cases) (Askeland et al., 2011).

For further theoretical understanding of the load-depth concept and elastic contact theories of indentations in polymers, refer to (Alisafaei & Han, 2015; Díez-Pascual et al., 2015; Gibson, 2014).

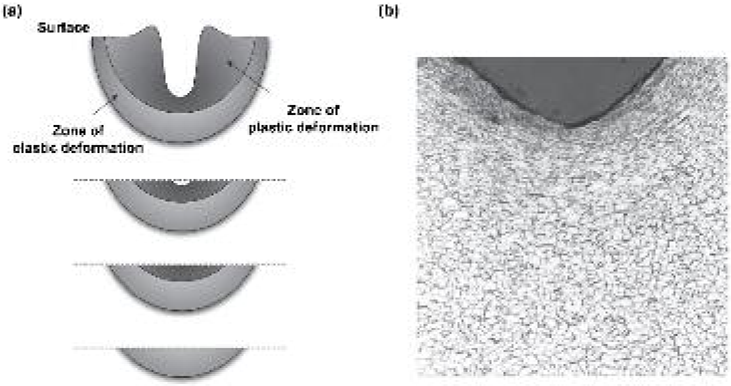


FIGURE 2 (a) Cross section of a stamped number in metal, showing partial (i.e. intact zone of plastic deformation) and full obliteration. (b) The metallographic microstructure (low alloy steel) of the serial number. After deformation, the shapes (textures) of the grains are changed, as it can be seen from the top of the photograph (bottom of the mark) to the bottom of the photograph (undisturbed metal). Reprinted (adapted) with permission from {Katterwe, H. (2006). Chapter 7: Restoration of serial numbers. In E. Stauffer & M. S. Bonfanti, *Forensic Investigation of Stolen-Recovered and Other Crime-Related Vehicles* (pp. 177-205)}. Copyright {2023} Academic Press, Elsevier Science.

4 OBLITERATION METHODS

Mechanical tampering is the most common method to remove visible contrast from marks (Katterwe, 2006). This can be accomplished by abrasion (e.g. scraping, hammering, filling) or stamping. As this step generally requires the preservation of the structural integrity of the firearm, the serial number may only be rendered superficially unreadable (i.e. invisible to the naked eye).

Other less encountered means of obliteration are possible, for instance thermal and chemical degradation. However, the extent of their effects and subsequent recovery remain under investigation.

5 RECONSTRUCTION OF OBLITERATED INFORMATION

A handful of methods for the reconstruction of alphanumeric characters in polymers, which exploit the generated structural heterogeneity and anisotropy, are proposed in scientific literature. These include chemical transformations by use of solvents to swell the surface, relief polishing usually performed by abrasion as well as heat treatment (Christen et al., 2013; Katterwe, 1994, 2006). Raman spectroscopy is also used to show residual strain for recovery purposes (Parisien et al., 2017; Parisien et al., 2019). Their use in a legal framework also requires these methods to be as non-destructive as possible, which allows for easy categorization.

5.1 Destructive methods

The ‘’classical’’ methods (i.e., most established) for polymers are derived from the reconstruction of serial numbers in metals (Katterwe, 1994) based on electrochemical etching. These techniques however present substantial disadvantages when considering the requirement of trace preservation, most notably their destructive nature. Lack of reproducibility and therefore reliability which arise from difficulties controlling the experimental parameters have also been reported (Christen et al., 2013). In addition to the experimental uncertainties, these destructive methods require certain knowledge about mechanical properties of the polymer for appropriate technique selection.

Chemical swelling

As the swelling capacity increases with the application of an external force, particularly compression (Conlan et al., 2011; Godbole et al., 2017; Katterwe, 1994, 2006), it is thus possible to observe a swelling contrast between the strained and unstrained regions of the sample (figure 3b).The mechanistic interpretation used to describe polymer swelling by solvents (e.g., formic acid, acetone, ethanol) is generally related to cross-linked polymers, specifically elastomers, such as rubber (Flory & Rehner, 1943; Mark, 1981). The process is governed by a driving force of enthalpic nature which can be explained by the Flory-Rhener theory (Flory & Rehner, 1943; Mark, 1981). Specifically, the diffusion of the solvent through the polymeric network generates a separation of the chains, reducing the intermolecular forces, therefore causing the enlargement of the polymeric structure (Godbole et al., 2017).

Heat treatment

This reconstruction technique relies on the local changes in crystallinity and density generated for example by mechanical stamping in the polymer structure. These affect the molecular relaxation and thus cause slight variations in the glass transition and melting temperatures between the strained and unstrained regions of the polymer (Christen et al., 2013; Conlan et al., 2011; Katterwe, 1994). This can thus lead to a slight elevation allowing for visualisation of the obliterated serial number, as shown in figure 3d.

This process sometimes refers to the memory effect by entropic elasticity, as heating to the glass point or melting point forces the chains of molecules to resume their initial deformation (increase in system entropy) (Christen et al., 2013; Conlan et al., 2011).

Relief polishing

Surface polishing exploits the local hardening of the material (Askeland et al., 2011) present due to significant residual strain, such as stretching or compression of the polymer, beyond its yield point. This hardening can result in structural heterogeneities when comparing the stressed and unstressed regions of the polymeric structure and therefore affects the polishing rates. A contrast allowing for the reconstruction of the serial number may therefore be observable, following the removal of layers of the material by relief polishing, usually performed by abrasion (figure 3e) (Christen et al., 2013; Katterwe, 1994, 2006).

The degree of hardening depends on several factors, such as molecular structure, molecular weight (especially the distribution of the molecules), cohesive energy, and morphology (i.e., the degree of crystallinity and branching of the polymer) (Askeland et al., 2011).

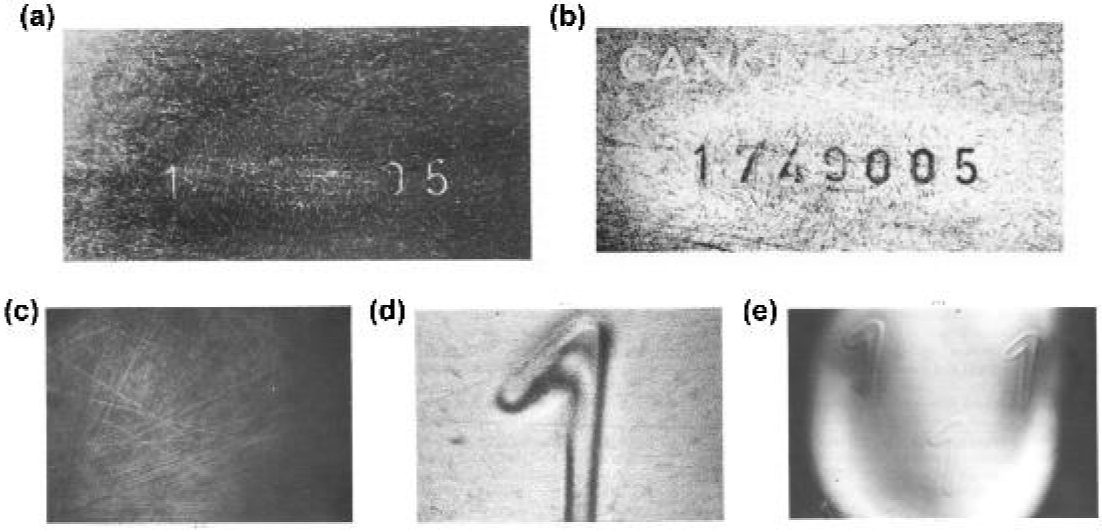


FIGURE 3. Erased number on a camera made from polycarbonate, (b) restored using ethyl ether as a swelling agent. (c) Obliterated marks in polyoxymethylene, restored by (d) polishing and (e) heating. Reprinted (adapted) with permission from {J. Forensic Sci. Soc., 1994, *34*, 1, 11-16 *Anal. Chem.* 2017, 89, 21, 11648–11652}. Copyright {2023} Elsevier Science.

5.2 Non-destructive methods

The relevance of developing non-destructive techniques relies mainly on trace integrity. This primarily allows for repeatability of the measurement in the near or distant future (e.g., in instances of counter-expertise or case revisiting).

Hyperspectral Raman imaging

As reported in previous studies (Parisien et al., 2017; Parisien et al., 2019; Skokan et al., 2022), hyperspectral Raman imaging has thus far proven to be the only non-destructive and effective (i.e. in terms of reproducibility and universally applicable) technique for the reconstruction of obliterated characters in polymers. This method requires a state-of-the-art experimental framework (i.e. high spectral resolution and considerable acquisition times) and a two-step mathematical fitting process for identifying relevant data.

Theory/Fundamentals

The Raman effect describes the inelastic scattering of light, specifically photons, following its interaction with matter (Smith & Dent, 2019; Toporski et al., 2010). This principle is used in Raman spectroscopy to measure the energy spectrum of phonons (i.e. quantized vibration modes) to establish chemical as well as structural information of the sample under investigation (figure 4).

Only chemical bonds that meet the selection rules, i.e. a molecular polarizability that changes along the normal vibrational mode with a non-zero gradient at the equilibrium geometry, will be active in Raman spectroscopy (Smith & Dent, 2019; Toporski et al., 2010). Therefore, this technique is complementary to the existing state of the art as it is not applicable to metals.

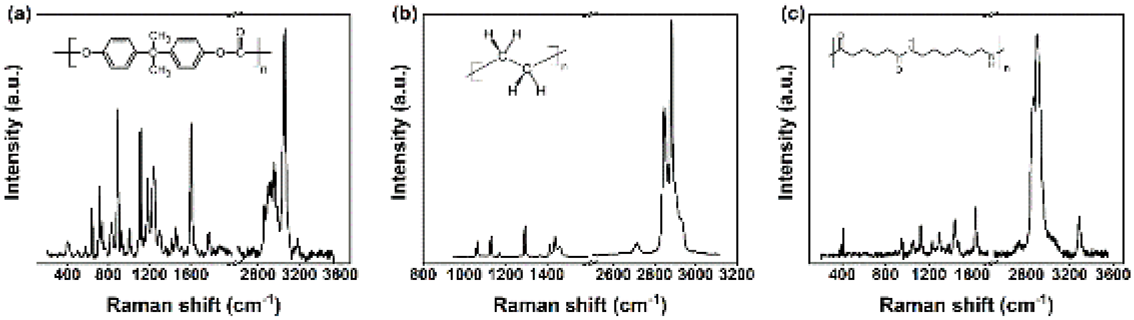


FIGURE 4 Typical Raman spectra and corresponding molecular structure of (a) polycarbonate, (b) polyethylene and (c) nylatron. Reprinted (adapted) with permission from {J. Raman Spectrosc., 2022, 52, 8, 1415-1427}. Copyright {2023} John Wiley & Sons.

Different parameters, notably the peak shift, the full width at half maximum (fwhm) and the intensity ratio, extracted from the Raman spectrum allow for the study of strain induced deformations.

Peak shift

The frequency shift provides information about the molecular binding energy and therefore interatomic distance of a given bond (Smith & Dent, 2019; Toporski et al., 2010). For that matter, the peak position is a function of strain.

For small molecular oscillations, it is possible to use the harmonic oscillator model, which describes a material point of mass m oscillating with a spring constant k proportional to the elongation (Atkins & De Paula, 2013). This approximation allows the energy of the system to be characterized by the potential energy equation as well as the angular frequency ω of the oscillation described below (Atkins & De Paula, 2013):

$$U(r) = U_0 + \frac{1}{2}k(r - r_0)^2 \qquad (1)$$

where U_0 is the equilibrium potential energy, r is the actual distance of the two atoms at a given time, and r_0 is the internuclear distance at vibrational equilibrium.

$$\omega = \sqrt{\frac{k}{m}} \qquad (2)$$

Introducing compressive strain will result in an increase of the restoring constant value (i.e., stiffer molecular bond). As this constant is related to the angular frequency of the oscillation (equation 2), which will also increase, the Raman peak will shift towards higher wavenumbers. This relative change is with respect to the molecular oscillation of same nature that has not been subjected to mechanical stress.

The same rationale holds true for the opposite effect (i.e. shift towards lower wavenumbers resulting from a decrease of k) is observable with the introduction of tensile strain (figure 5).

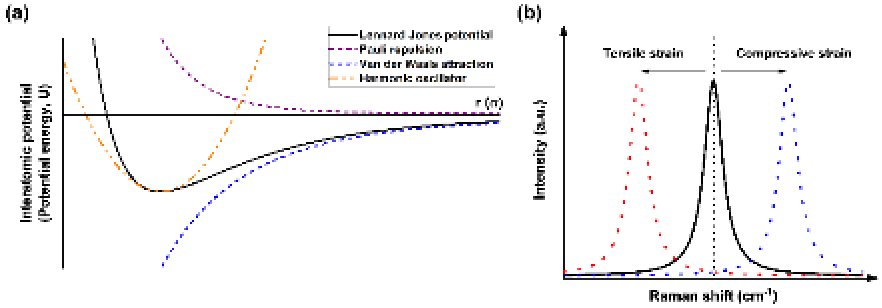


FIGURE 5 (a) The Lennard-Jones potential, a model of intermolecular potential energy that includes attraction and repulsion interactions as well as the harmonic oscillator approximation. (b) The effect of mechanical stress resulting in strain on a given Raman peak shift.

Full width at half maximum (fwhm)

The full width at half maximum of the Raman peak can be associated with the inverse phonon lifetime. The latter is relevant because it provides information about the crystallinity and structural orientation (with respect to the polarisation direction of the incident beam), specifically by describing the harmonic and anharmonic interactions of the molecular system (Toporski et al., 2010).

The phonon lifetime in solids is limited (i.e., damping of the molecular oscillation), in part due to phonon-phonon interactions, but also to scattering by defects or deformations in the crystalline structure (e.g., induced by strain). In fact, a decrease in the amplitude of the oscillation, as a result of the damping, leads to the broadening of the associated Raman peaks (figure 6) (Bergman et al., 1999; Joya et al., 2014).

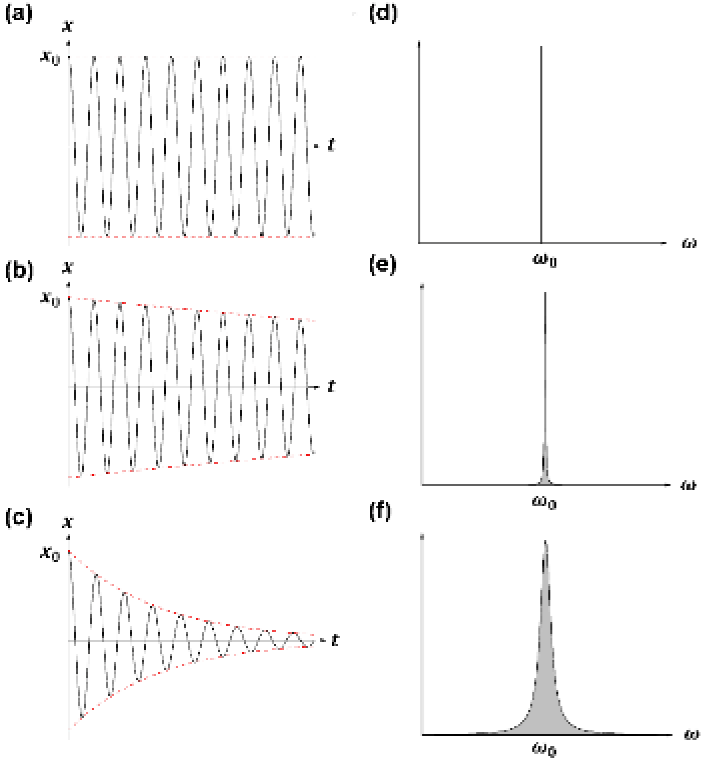


FIGURE 6. The phonon lifetime and corresponding full width at half maximum of a Raman peak in the case of (a) a perfect crystalline, (b) a semi-crystalline and (c) an amorphous structure. The frequency (ω) of the emitted radiation of amplitude x is no longer monochromatic (delta function) for the last two structures as was the case of the perfect crystal.

Reconstruction methodology

The studies conducted by hyperspectral Raman imaging (Parisien et al., 2017; Parisien et al., 2019; Skokan et al., 2022) involved the analysis of polycarbonate, polyethylene, nylon, and nylatron samples. This technique allows for the combined acquisition of spatial and spectral information Data is therefore collected as a three-dimensional datacube. The character of interest, a 0,5 x 0,6 cm^2 letter " H " was introduced by manual cold stamping each of the polymeric structures. A partial obliteration, specifically the right side of the character, was achieved using a mechanical milling machine (as shown in figure 7a).

The approximate marking and obliteration profile depths were respectively as follows: 120 µm and 200 µm for polycarbonate, 230 µm and 320 µm for polyethylene, 120 µm and 180 µm for nylon as well as 85 µm and 135 µm for nylatron. These numbers correspond to the North American serial number requirements stated above.

The reconstruction method was developed and proposed in three distinct steps. Identification of the polymer by analysing the Raman bands (figure 7b) was first performed. These are compared with the Raman modes reported in literature to confirm the assignment. Identification of the strain sensitive bonds is then conducted. A line scan in the visible portion of the character, specifically perpendicular along the horizontal axis of the letter "H" (illustrated by the red dashed line in figure 7a) is acquired. As the expected deformations are in the range of 1 to 2 wavenumbers (i.e. at the borderline of most hardware resolutions), enhancement by mathematical approach is necessary.

To gain precision on the position of the peak maximum, a mathematical modeling procedure of each peak composing the spectrum is carried out. The Lorentzian function[1] was chosen for this step, as it takes into account the intrinsic behavior of the molecular bond, i.e. allows for modelisation as a damped harmonic oscillator [(Atkins & De Paula, 2013; Bradley, 2007; Yuan & Mayanovic, 2017). This function with a symmetric profile is characterized by the initial amplitude (Y_0), the area under the curve (A), the full width at half maximum (w) and the central position of the peak (x_c) and is stated as follows (Atkins & De Paula, 2013):

$$Y(x) = Y_0 + \frac{2A}{\pi} \frac{w}{4(x - x_c)^2 + w^2} \tag{3}$$

As stated, the main objective of this step is to increase the accuracy of the extracted values (e.g. peak position, full width at half maximum, intensity) by pushing the instrumental limit. The evolution of these parameters along the linear scan is analyzed to identify the strain sensitive bonds in each of the polymer structures (figure 7c, d). The plot in figure 7d is an example of a Raman band affected by the initial stamping procedure (i.e. giving rise to residual strain of the compressive type). Indeed, the central portion of the graph shows a shift of the Raman peak towards lower wavenumbers in comparison to the position of the band in the unstrained regions.

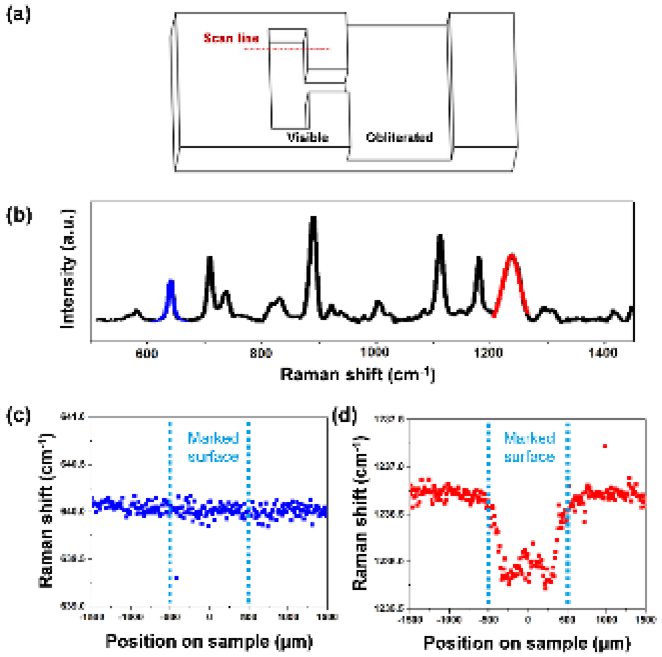


FIGURE 7 Identification of strain sensitive Raman bands. a) Representation of the polymer sample showing the visible (left) and obliterated (right) parts of the stamped character. The red dashed line corresponds to the area of interest used for the line scans. b) Raman spectrum of polycarbonate acquired in the stamped (non-obliterated) zone of the sample. c) Position of the blue Raman peak as a function of the location on the sample. No significant variation is detected. Spectral bands that are not sensitive to mechanical stress will show a similar profile. d) Variation of the position of the red Raman band indicating the presence of tensile residual strain (i.e. shift to lower wavenumbers) and therefore an exploitable feature. Figure courtesy of Cédric Parisien.

A pixel-by-pixel Raman acquisition is then conducted over the full area of interest (i.e. the character and surrounding regions). This generates a map (matrix) of the region in question allowing for exploitation of the detected variations for each parameter of the spectrum (i.e. peak position, fwhm, intensity ratio). This matrix, is then associated to a colour scale, therefore allowing for visual emphasis of the possible contrast between the stamped and unstamped areas of the sample (figures 8 and 9). It is worth mentioning that the same mathematical process (i.e. described for the identification of sensitive bonds) is used to extract the relevant data.

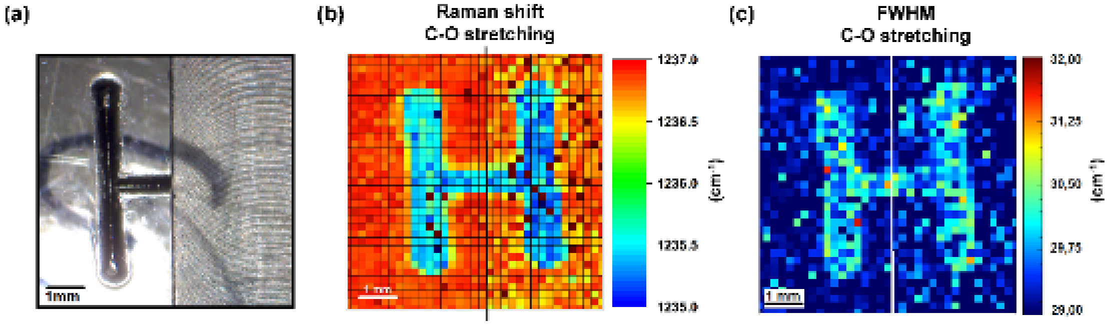


FIGURE 8 Spectral images of (a) the shift and (b) the full width at half maximum of the C−O Raman peak of polycarbonate showing the successful recovery of the obliterated right part of the letter. Reprinted (adapted) with permission from {*Anal. Chem.* 2017, 89, 21, 11648–11652}. Copyright {2023} American Chemical Society.

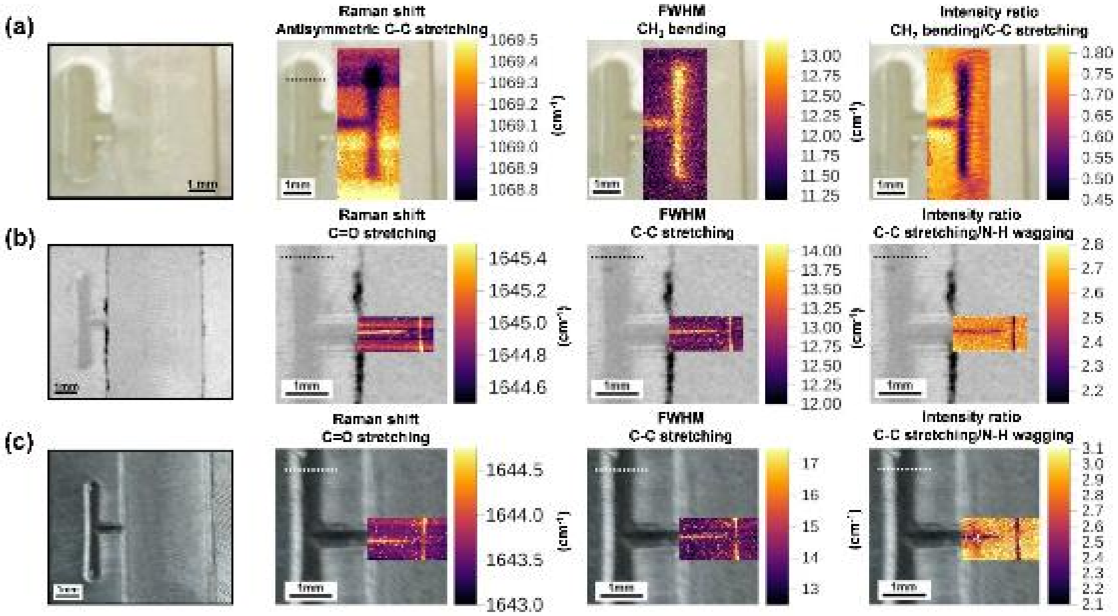


FIGURE 9 Spectral images of the peak shift, full width at half maximum, and peak intensity ratio of (a) polyethylene, (b) nylon, and (c) nylatron. The left part corresponds to a picture of the sample, while the right map presents the spectral image over the obliterated region, showing the successful recovery of the abraded section of the “H”. Reprinted (adapted) with permission from {*Anal. Chem.* 2019, 91, 22, 14247–14253}. Copyright {2023} American Chemical Society.

Intensity and depolarisation ratios

Studies have also reported a change in peak intensity ratios (Parisien et al., 2019). As these variations resulted from both an increase and decrease in the intensity of some peaks, the hypothesis associated with bond breakage causing a reduction in the population of Raman oscillators had been ruled out as a primary explanation.

In fact, variations in intensity can occur as a result of changes in the polarization of the Raman band thus from the modification of the polarizability tensor (i.e. symmetry of the molecular oscillation). The origin of these variations can be experimentally measured and detected through the depolarization ratio. These intensity variations can also involve the relative rotations of the chemical bond or chemical entity that leads to the Raman band.

For further understanding and discussion on the provenance of these intensity variations, readers can refer to (Allemand, 1970; Frisk et al., 2004; Porto, 1966; Skokan, 2022; Skokan et al., 2022).

Depth of strain propagation

The propagation depth of the initial impression in the polycarbonate sample (i.e. impression depth of ≈ 120 µm introduced with a force estimated to be ≈ 169 MPA) was also studied using hyperspectral Raman spectroscopy (Parisien et al., 2017). The cross-section of the unobliterated letter ‘’H’’ showed residual strain from the initial impression to be about 750-800 µm deep into the substrate (figure 10). The sensitivity of the technique therefore allows for detection of the character even if the relief is highly affected (obliteration depth of ≈ 80 µm to render it invisible to the naked eye).

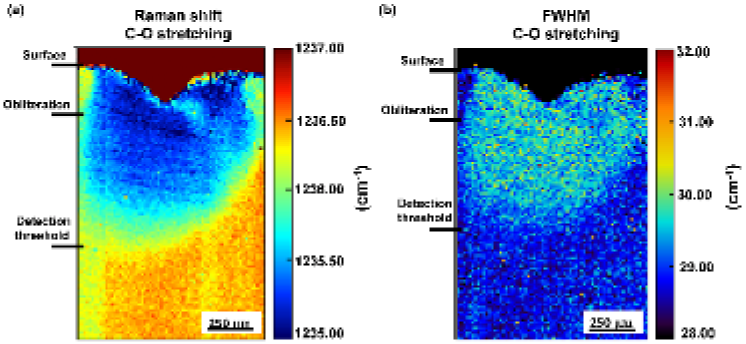


FIGURE 10 Spectral images of (a) the shift and (b) the full width at half maximum of the C−O Raman peak, acquired on the cross-section of a letter marked on the polycarbonate sample. Reprinted (adapted) with permission from {*Anal. Chem.* 2017, 89, 21, 11648–11652}. Copyright {2023} American Chemical Society.

Statistical characterisation of the reconstruction

An evaluation of the obtained contrast was proposed by characterising the distribution of the set of pixels composing each map by means of histograms. This analysis was performed on the pixels corresponding to the position as well as the fwhm parameters of the Raman peaks (Parisien et al., 2017; Parisien et al., 2019). Gaussian functions with identical sigma (σ) are then applied to the respective distributions (figure 11). It is worth mentioning that this function was selected on the basis of two hypotheses, notably that two distinct pixels populations are present (i.e. the strained and unstrained) and that both are distributed equally on either side of the mean (assuming only a systematic error rate from the instrumental configuration).

This characterisation leads to the identification of two distinct pixels populations separated by at least 2σ, thus meaning that 95% of the pixels are confined to their respective populations (Mishra & Datta-Gupta, 2018) for the four studied polymers (Parisien et al., 2019).

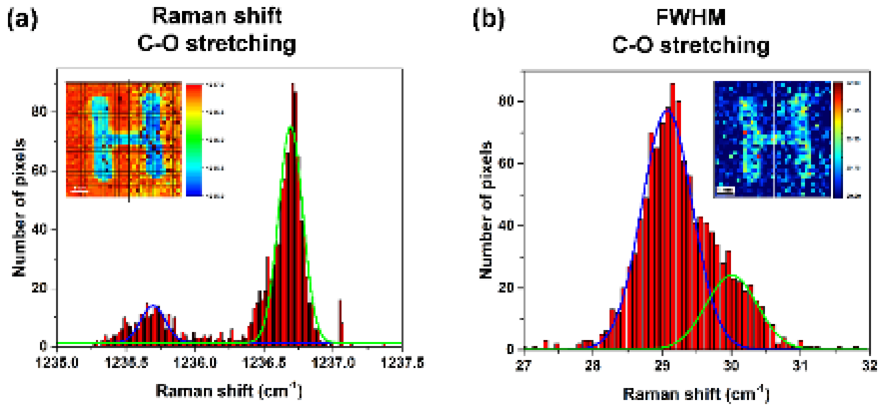


FIGURE 11. Histograms illustrating the populations of strained and unstrained pixels for the (a) peak shift and (b) full width at half maximum of the C-O stretching bond. The solid blue and green lines represent the numerical fits for two Gaussian distributions assuming identical σ in each respective case. Reprinted (adapted) with permission from {*Anal. Chem.* 2017, 89, 21, 11648–11652}. Copyright {2023} American Chemical Society.

It is important to note, however, that this analysis does not take into account the location of the respective pixels in the maps. To add quantitative significance, it would be relevant to incorporate pattern information (i.e. configuration of the pixels) of the alphanumeric character in order to establish a global appreciation of the letter (i.e. consideration of the nature and thus the particularity of the trace in question).

The statistical analysis could, for example, be executed in two steps: a) by characterising the pixels distribution through consideration of their value (e.g. intensity on an 8-bit scale from 0 to 255 or from black to white) and b) by incorporating the value of neighboring pixels in order to exclude random distributions. This last step could be done by interpolation methods (e.g. bicubic or bilinear) or by any other form of mask (e.g. convolution matrix or kernel) used for image processing (e.g. for smoothing, sharpening).

Multivariate statistical approach

The proposed Raman method (Parisien et al., 2017; Parisien et al., 2019) initially required a nontrivial two-step mathematical fitting process for identifying and extracting relevant data. This procedure additionally entails acquired knowledge in regard to material sciences for the adequate selection of the mathematical functions (i.e. depending on the nature of the molecular oscillations and hardware influence). Although functional, the data processing was a tedious step and therefore limited the possibilities of large-scale deployment for use in a forensic science context.

Principal Component Analysis (PCA) applied to hyperspectral Raman data was studied (Skokan et al., 2022) as a potential solution. This unsupervised method extracts pertinent variance from the combined strain induced peak shift, full width at half maximum and intensity ratio variations from the complete Raman spectrum. Scores matrices showed distinct visual contrast between strained and unstrained regions (figure 12) allowing for optimized results in comparison to those previously stated with the mathematical fitting procedure. Normal density functions and Receiver Operating Characteristics (ROC) curves were used to assess statistical significance of the classifying ability of the score matrices. Furthermore, as this approach seemingly maximizes the separation of the distributed pixels based primarily on intensity ratio variations, partial acquisition of the spectrum as well as reduced acquisition times can be considered.

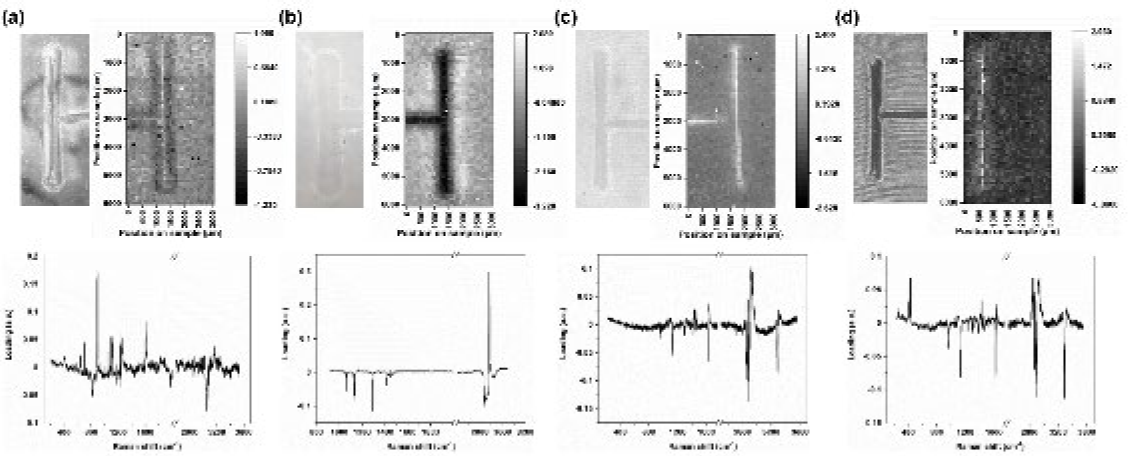


FIGURE 12 Reconstructed character based on score matrices (top) and corresponding loading plots (bottom) for (a) polycarbonate (PC 6), (b) polyethylene (PC 2), (c) nylon (PC 6), and (d) nylatron (PC 5). Reprinted (adapted) with permission from {J. Raman Spectrosc., 2022, 52, 8, 1415-1427}. Copyright {2023} John Wiley & Sons.

Experimental requirements

To achieve successful recovery of serial numbers in polymers by Raman imaging, some experimental conditions are essential. It is important to mention that this section targets the specific necessities for the analysis of alphanumeric characters. Other references (Smith & Dent, 2019; Toporski et al., 2010) should be consulted for minimal hardware requirements for conducting general Raman spectroscopy measurements.

First and foremost, the instrumental configuration must possess mapping capabilities. For the purpose of image acquisition, a sample scanning configuration is preferable to beam scanning options as the latter implies changes of the optical access at every pixel. The stability of common scanning stages largely exceeds the requirements for imaging with tens of micron resolution for any reasonably stable temperature (e.g. avoiding exposure to sunlight). The use of two-dimensional charge-coupled device (CCD) detectors allows for vertical binning, a feature that is not available even for science grade complementary metal-oxide-semiconductor (CMOS) detectors. Vertical binning, i.e. the hardware-implemented summation over pixels with the same spectral information, drastically improves the signal-to-noise ratio. Additionally, this pixel-by-pixel construction requires sufficient spatial resolution (i.e. size of each pixel) and pixels density to avoid undersampling the surface of interest. As the propagation width of the deformation is dependent on the nature of the polymeric structure, precisely the elastic modulus, this criterion will vary from one polymer to another (Parisien et al., 2019; Skokan et al., 2022). Previous studies, which used optical character recognition (OCR) algorithms as a baseline, have shown adequate recovery with spatial resolutions as low as 100 dpi on polycarbonate, 200 dpi on polyethylene as well as 300 dpi on nylon and nylatron (Parisien et al., 2017; Parisien et al., 2019). It has been stated that the spatial resolution required for reconstruction purposes is inversely proportional to Young's modulus of the given polymer (Parisien et al., 2019). These numbers may however need to be reconsidered in cases where only partial characters are recoverable (i.e. reassessment of the evidential value of the recovery should be conducted).

Spectral resolution is also an important factor to consider. As denoted above, variations of peak shift and fwhm are below 1,5 cm^{-1} in the considered cases. In order to produce the optimal contrast between the strained and unstrained regions of a given character, the experimental configuration should be capable of detecting these small changes. Therefore, a spectral resolution (hardware resolution) in the order of 1 cm^{-1} (or lower) is optimal. Mathematically fitting the data and principal component analysis do allow some leeway.

All reported Raman measurements have been conducted using a 488 nm laser and required acquisition periods of several hours per character (Parisien et al., 2017; Parisien et al., 2019;

Skokan et al., 2022). This allowed for the use of a high energy laser while still remaining in non-resonant conditions (i.e. the energy is lower than the conduction band of the polymers, therefore the excitation level remains in the band gap of the material). The experiments however are theoretically possible with other laser wavelengths, for instance 514, 532, 633 and 785 nm (i.e. more commonly encountered in forensic laboratories). The energy of these lasers is sufficient to excite the molecular vibrations of interest yet come at the cost of Raman cross-section. As the scattering intensity is inversely proportional to the 4th power of the illumination wavelength, using longer wavelengths results in a decreased Raman signal (Smith & Dent, 2019; Toporski et al., 2010).

It is noteworthy to mention that Raman spectroscopy is a non-destructive technique as it does not require sample modification. However, experts should resist increasing laser powers and acquisition times that would exceed the destruction level threshold of the polymers (i.e. avert thermal degradation and local thermal expansion).

Surface roughness is also worth mentioning as inhomogeneous obliteration remains a high possibility. As the main goal of the criminal activity is to render the serial invisible to naked eye, the obliteration will be conducted in an uncontrolled manner with tools at hand (i.e. specimen rather than sample in a real life scenario). Many Raman configurations are equipped with auto-focus options allowing for small variations (i.e., within the focal depth of the objective) of the analysed surface of interest. As a general rule, using high numerical aperture objectives does allow for higher solid angles of collection, but lowers focal depths (in the range of 5 µm). However, as strain propagation largely extends under the initial relief, focussing into the sample can be a great way to counter interfering surface inhomogeneities.

6. OUTLOOK

Despite the fact that hyperspectral Raman spectroscopy has shown successful results for the reconstruction of stamped serial numbers in polymers, a few challenges pertaining to the technique as well as to the sample remain. As the aforementioned method is most notably time consuming (i.e. trade-off between scattering efficiency and laser power) with acquisition times of several hours per character, investigation of other non-destructive techniques are preferable for large scale deployment. Thoughts on the necessary interpretation of the results (i.e. quantification of their significance), using a framework relevant to forensic science, are also discussed.

6.1 Optimisation of data acquisition

Although functional and non-destructive, the Raman method is unsuitable in cases where time sensitive information is required, as detection of peak shift and fwhm variations can be time consuming (mainly due to the necessary signal to noise ratio). To increase the ease of detection of structural and chemical variations between the strained and unstrained regions of the polymeric samples, it is relevant to consider analytical methods exploiting intensity signals. This allows higher sensitivity, which leads to lowered acquisition times and spectral resolution.

6.1.1 Fluorescence imaging

Is it possible to exploit fluorescence signature variations of polymers in response to the introduction of a mechanical stress, such as the stamping of a serial number? This idea arises from a simple experiment that can be performed with a black plastic cable tie. Following the introduction of a fold, a whitening of the fastener is visually perceptible in the area having undergone the stress. A variation of the absorption in this region is thus highly plausible.

Fluorescence is a phenomenon involving the rapid emission of light following the electronic excitation, usually by photon absorption, of a molecule or an atom (thus occurring from electronically excited states) (Lakowicz, 2006). It is in fact an instantaneous emission (of the order of 10^{-9} to 10^{-6} s) due to the transition between two states of same multiplicity, for instance from the excited singlet state S_1 to the fundamental singlet state S_0. Fluorescent emission spectroscopy is known to be a favourable technique for the detection of deformation and mechanical damage (change in structural stiffness) in polymeric materials (Li et al., 2016).

Exploitation of the auto-fluorescence signature would constitute a new approach as it allows for wide-field imaging. This would offer greater throughput and is currently unavailable with Raman spectroscopy (i.e would require the use of tunable filters with a cutoff precision in the order of 1 cm^{-1}).

6.1.2 Brillouin Spectroscopy

From a quantum physics perspective, much like the Raman effect, Brillouin scattering is an interaction between an electromagnetic wave and a density wave (i.e. inelastic photon-phonon scattering) (Palombo & Fioretto, 2019; Patterson, 2006). Acoustic vibrations, generated by the thermal motion of atoms in a given material, lead to density variations and thus scattering of incident light (i.e. low frequency phonons).

The frequency of the photon can be described by the following relationship (Patterson, 2006):

$$\Delta\omega = \nu_s \frac{2n\omega}{c} \sin(\theta/2) \tag{4}$$

where vs is the acoustic wave velocity (speed of sound in the given medium), n is the refractive index, ω is the phonon frequency, and θ is the angle of incidence (or scattering angle).

A previous study involving the use of acoustic phonons, specifically the frequency of scattered photons, was used to determine the crystallinity length within a polymer (i.e. evaluation of the vibration propagation of polymer chains) (Bartczak & Kozanecki, 2005). It is thus plausible to believe that the introduction of characters into polymer structures could induce a change in density and therefore influence the elastic properties of the material that would be detectable in Brillouin spectroscopy. This would allow for a visible contrast between the strained and unstrained areas of the polymer as a result of the imaging process.

The main question, still under investigation, remains the evaluation of the sensitivity (including parameters such as spectral resolution, signal to noise ratio and acquisition time) necessary for the detection of such variation. New instrumental configurations, employing virtual imaged phase arrays (VIPA) in replacement of the classic Fabry-Perot interferometer (i.e. optical dispersive components)[2], do allow for increases transmission efficiency (Palombo & Fioretto, 2019) and therefore reduce the acquisition time of hyperspectral maps.

6.2 Relevant and necessary interpretation framework

Most of the published studies focus mainly on the development and the optimisation of reconstruction methods from a technological (or practical) standpoint without considering the adequate and necessary reasoning skills to reconstruct the information of the trace (Roux et al., 2021), in this case the recovered serial number. In fact, the criteria used to qualify the reconstructions as successful in many studies remain ambiguous. Most seem to solely rely on visual observations while stating difficulties controlling the experimental parameters and therefore the reconstructions. This leads to unanswered influence of cognitive biases in previously published studies (e.g., reporting a ‘’successful’’ reconstruction with the knowledge of the serial number having been obliterated), as well as questions about the applicability of the method in a real case.

These considerations are especially pertinent for partial restitutions. Alphanumerical characters possess a specific form and arrangement allowing for their recognition. Hence, what number and configuration (i.e. location) of pixels, for example, enables identification of a given character? Some scholars have proposed the use of OCR algorithms as baseline parameters (Parisien et al., 2019). Such systems call for binarisation, therefore requiring an optimal cut-off range. Their accuracy thus largely depends on the quality of the input image (Chaudhuri et al., 2017).

This type of approach encompassing the uncertainty dependent of the quality of the restoration and the complexity of each restored figure should be characterized within a probabilistic inference framework of Bayesian nature.

As the use of artificial intelligence is increasingly being discussed in many scientific fields, including in the forensic science community, it is interesting to consider the extent of this tool and its application for the reconstruction of obliterated characters.

Merging AI and the need for a Bayesian inferential decision process could be a promising challenge to secure serial number restoration. Machine learning systems (such as unsupervised dimension reducer and clustering algorithms) could be applied for data processing and relevant signal recognition, specifically for rapid detection and extraction of pertinent variations (e.g., between strained and unstrained areas of the sample), defining a cyclic process which permits significance evaluation of the "raw" signal and retrospectively better understanding of basic theory and principles. Finally, the Bayesian framework applied to the analysis of generated images would assess the likelihood ratio of a specific alphanumeric figure over all its alternatives. For instance, quantifying the probability of observing the image if the character is an " H " over the probability of observing an ” H ” if it isn’t one. It is worth noting that this construction would require extensive acquisition of data of various qualities. The *plus-value* of such an evaluative process has to be balanced by considering that the reconstructed serial number is likely to have been utilized in the investigative stage (i.e. when there is a certain leeway with the number and level of certainty of the working hypotheses) leading to the final expertise.

Sidebar: The synergy of forensic science

This publication highlights that the scientific study of the trace, specifically the recovered obliterated mark, necessarily requires, amongst other things, a good comprehension of material science knowledge to properly assess and conduct the reconstruction.

The fundamental understanding of the mechanisms involved in the creation of the serial number as well as the resulting effects in the material (i.e. polymer, metal) however bear meaning when combined with the proper interpretative framework (i.e. when considering the singular past of the obliterated number). Further proving that ‘’ the main driver for the development of forensic science should actually not reside in the standardisation of processes (borrowed from other disciplines). It should rather focus on a better understanding of basic forensic theory and principles ’’ (Roux et al., 2021).

6.3 New forensic challenges

Strain detection in polymers has thus far proven useful for the reconstruction of stamped serial numbers in firearms. Expanding the field of application to the restoration of QR codes and laser induced marks would account for new trends in terms of weapon marking (Paoli, 2015). *Exploitation of carbonisation and densification of the local polymer structure, resulting from laser induced effects, is promising. Heat-affected zones will greatly depend on the power and width of the laser pulse as well as the thermal conductivity and crystallisation ability of the polymer in question. A few* studies have studied depth analysis of laser induced markings and have reported penetration depth in the range of a few 100 nanometers (Dunn & Ouderkirk, 1990; Fritzsche & Pretsch, 2012; Savu et al., 2013).

Addressing additional forensic challenges, would however, be the logical step forward in expanding the established synergy between material and forensic sciences. New relevant applications of strain detection in polymers could include failure analysis in polyvinyl chloride (PVC) or acrylonitrile butadiene styrene (ABS) pipes for corroboration of activity level information as well as analysis of fractured 3D printed objects (e.g. firearm barrels, knives) for added evidential value to physical match. Experimental requirements for these types of analyses will have to be reconsidered, as these objects are most probably curved. Method evaluation and relevance will strongly depend on the length scale of pertinent fracture propagation. It is worth mentioning that these new avenues strengthen the need for a relevant interpretative framework, as there is no database to rely on for validation (as is the case for serial number reconstruction).

7. CONCLUSIONS

Optical spectroscopy, in particular Raman imaging, has paved the way for the non-destructive recovery of serial numbers in polymers based on the detection of residual strain. The technique is universally applicable to all polymers and exploits variations of certain peak positions, full width at half maximum and relative peak intensities of the vibrational signature of polymers. The initial numerically intense data fitting procedure has already progressed towards a more efficient treatment via principal component analysis, an unsupervised method (i.e., pre-existing knowledge about the sample and data set is not necessary). With a detection sensitivity that largely exceeds the requirements for the recovery of mechanically introduced serial numbers, work is in progress to deploy the technique to thermally introduced reliefs.

In terms of data acquisition speed, Raman spectroscopy suffers from a notoriously low cross-section. Along with the obligation to keep the laser intensity below the destruction threshold of the sample, acquisition periods of several hours per character are typical. Other optical contrast mechanisms including fluorescence are under consideration as they could potentially allow for faster data acquisition. In regard to the data analysis, the use of correlative tools based on optical character recognition, for example, could improve the statistical significance of patterns. The exploitation of deep learning algorithms, even though under heavy debate in terms of admissibility, may provide valuable guidance to practitioners about whether exploitable information is hidden in the hyperspectral stacks (which could then be exploited with the aforementioned techniques).

The development of serial number reconstruction and to a greater extent residual strain exploitation of polymer traces should therefore not only rely on the optimisation of non-destructive analysis methods, but also on the application of an interpretative framework specific to the forensic context, especially when it is used to justify the rationale of the technique being developed. Optical spectroscopy has opened new perspectives to the recovery of obliterated serial numbers in polymers. Further investigation can potentially lead to a sufficiently user-friendly method, enabling deployment to even a non-expert community.

AUTHOR CONTRIBUTIONS

Lilian Skokan: Conceptualisation (equal); writing – original draft (lead). **Frank Crispino:** Conceptualisation (equal); writing – review and editing (equal). **Cyril Muehlethaler.** Conceptualisation (equal); writing – review and editing (equal). **Andreas Ruediger:** Conceptualisation (equal); writing – original draft (supporting).

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CONFLICT OF INTEREST

The authors have declared no conflict of interest for this overview.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study. Data is cited and available through the references.

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ENDNOTES

[1] A Voigt profile, defined as the convolution of Lorentzian and Gaussian functions, is sometimes preferred for processing spectroscopic data as it accounts for parasitic effects. However, the peak broadening that can be instrumentally generated (e.g., from the grating, excitation source, detector) was of little consequence in the case of this study. The use of the Lorentzian function for mathematical modeling was therefore adequate.

[2] For additional information regarding Virtual Imaged Phase Array's (VIPAs) and Fabry-Perot interferometers, readers can review (Patterson, 2006)the following references: (Palombo & Fioretto, 2019)

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