Brand Protection and Authentication Enabled By Frangible Polymer Technology

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ABSTRACT

Tetramer has developed and patented a unique technology to produce pre-stressed frangible, polymeric coatings [1]. These can be applied using traditional thin-film coating and curing techniques or more advanced 3D-printing methods. The ability to produce stable, pre-stressed films allows for superior tamper indicating coatings as the films not only crack in the area where the coating has been breached, but continue to propagate across the entire surface of the coating. These films can also be customized with pre-defined crack patterns and crack densities that enable manufacturers to apply unique and individualized strategies for product authentication and anti-counterfeiting. Tetramer has demonstrated the performance of coatings on test substrates, in both active and passive configurations.

Keywords: brand protection, frangible, tamper-indication, authentication

1 INTRODUCTION

Technologies for printing and additive manufacturing have advanced at exponential rates while their costs have dropped, making them more accessible to consumers [2]. This development has provided tools for the general public to produce 2D and 3D media and prototypes with greater complexity and quality and in a greater variety of materials for numerous industries such as construction and dentistry [3, 4]. Concurrent with lawful applications of such technologies has been their use for illicit activities such as counterfeiting currency and brand name products by spoofing authentication technologies [5]. Novel tamper-indicating and authentication technologies are needed to combat counterfeiters and protect supply chains.

2 BACKGROUND

The term “frangible tamper labels” is commonly used for cellulose film-based, tamper-indicating adhesive labels that disintegrate during an attempt to physically remove them from a substrate. The lack of cohesive strength that makes these materials useful for tamper indication also limits their range of applications. Tetramer has developed an advanced frangible material system that can be used to prepare both 2D and 3D samples with better mechanical strength and an enhanced tamper-indication mechanism based on optically transparent polymers. The monomer precursor material is a liquid at room temperature, which enables a variety of 2D printing techniques, but its viscosity can be modified to enable additive manufacturing methods as well. Transparent films that catastrophically and reproducibly fail in a predetermined manner allows for three types of products be developed: (1) frangible waveguiding coatings including an LED and sensor to detect penetration of the coating, (2) single-use authentication tokens with predefined crack patterns, and (3) frangible coatings which obviously demonstrate when they have been physically breached.

While initially developed as tamper indicating coatings for the DOE, current commercial efforts focus on producing a simple, easy-to-use authentication tag for commercial consumer products. The initial concept of operation is to produce frangible tags with specific patterns or crack densities that are pre-defined during their manufacture. The patterns are not visible and the active portion of the tag appears as a transparent window until the end-user activates the franging mechanism to reveal the pattern. Based on fundamental understanding of the materials and processing parameters as well as extensive empirical analysis, Tetramer can accurately predict the types of crack patterns and density of cracks that are produced under various processing conditions.

2.1 Pre-Stressed Polymer Coatings

The precursor material for the frangible coatings can be cured via thermal or UV processing, and upon curing it hardens to become brittle and pre-stressed. The precursor has a high rate of shrinkage and the coating begins to reduce in volume as the polymerization proceeds [6]. The surface of the coating cross-links first and stiffens which restricts flow of the material as it shrinks. This results in compressive forces between the molecules at the surface of the coating (Figure 1). Precursor material in the center of the coating continues to shrink as it cures but is flow-constrained by the cross-linked upper surface and the adhesion of the lower surface to the substrate.

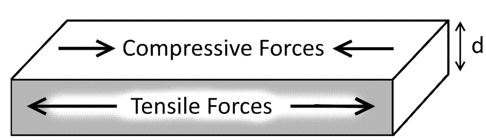

Figure 1: Cross-sectional diagram of a frangible coating illustrating regions of compressive and tensile forces.

This restriction of the shrinkage produces high tensile strain between the molecules in the center of the coating as it cures and results in a stress gradient across the coating thickness *d* and horizontally in the x-y plane. The stresses are locked into place as the residual monomers cross link and potential energy *U* is stored in the coating in the form of molecular strain, (1)

$$U = \frac{1V}{2E}\delta^2 \tag{1}$$

where *V* is the volume of material, *E* is the Young's Modulus of the cured polymer, and δ is stress. From equation (1), the amount of potential energy stored in the system is directly proportional to the volume of material and the square of the induced stress.

This system is similar to tempered safety glass where heat treatment and tempering of the glass results in large compressive forces at the surface and large tensile forces in the center of the glass. A benefit of the compressed surface molecules in both the glass and polymer systems is an enhanced hardness and impact resistance [7, 8]. Also similar to tempered safety glass, pre-stressed frangible polymer coatings crack catastrophically when a stress concentrator is introduced to their volume. Without a concentration point, the strain is distributed evenly across the coating; however, the presence of an inclusion, hole, or other perturbation to the cross-linked molecular matrix provides an initiation point, or crack tip for cohesive failure of the material. The presence of a crack tip enables the potential strain energy stored in the coating to be expelled as fracture energy U_f, the energy required to create new surface area in the material in the form of cracks [9]. The method used for the introduction of a stress concentrator sufficient to initiate crack propogation is generally negligible, meaning that any type of penetration of the coating surface should result in a franging event, regardless of the impact or force applied to create the penetration.

2.2 Pre-Determined Frangibility

Because crack formation is the primary release mechanism for energy stored in the films, the franging process is heavily influenced by the amount of stored potential energy for a given coating dimension. Higher levels of strain energy in the polymer matrix are balanced by releasing more U_f during the franging process. Larger values of released U_f produces more new surface area in the material which manifests as higher crack density per unit area of a frangible coating.

Working from Eq. (1), Tetramer has developed a set of processing parameters to control the density and and patterning of these frangible polymer coatings. Based on initiator concentration, thickness, and other parameters, the intensity and shape of the crack patterns can be pre-defined during their manufacture. Figure 2. illustrates the range of crack pattern types available with standard processing of the coatings. Additionally, the density of the crack patterns can be further tailored, resulting in significantly larger numbers of smaller cracks.

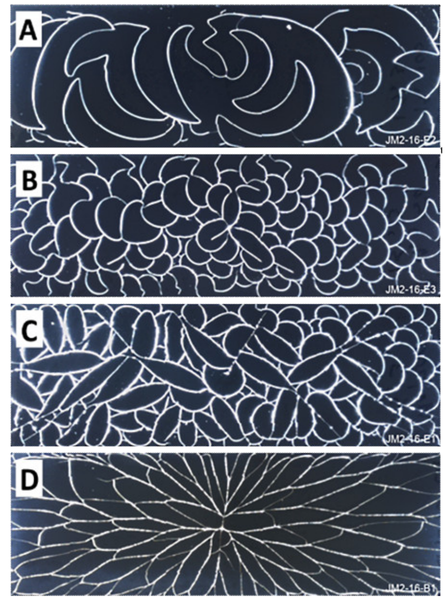

Figure 2: Images of franged polymer coatings with engineered types of crack patterns based on processing of the films. Standard processing can be used to tailor the crack patterns from a wave A) to a bubble B), mixed bubble/chaotic C), or petal pattern D).

Tetramer has also developed spatially pre-defined crack patterns that can produce distinct regions of higher and lower crack densities. This can be used to "write" patterns such as numbers or logos into the coatings that are covert until the coating is franged. Figure 3 illustrates a hand-deposited Venus symbol in a pre-stressed coating. Note the high crack density in the patterne d region that indicates a significant amount of stress was stored in these regions of the film.

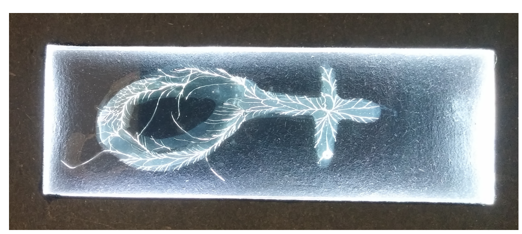

Figure 3: Spatially pre-defined Venus symbol in a frangible film.

2.3 Waveguiding Properties

The optical properties of these polymers has also been leveraged to provide additional functionality for tamper-indication purposes. Similar to waveguiding in fiber optics, transparent planar materials may be used to guide optical signals across their x-y dimensions. The frangible polymers developed by Tetramer have been demonstrated to be effective planar waveguides for visible wavelengths of light. Key design parameters for the coatings required that the refractive index of the polymer coating core n_2 (Figure 4) be $n_1 < n_2 > n_3$, where n_1 and n_3 are the refractive indices of the upper and lower clad materials, respectively [10].

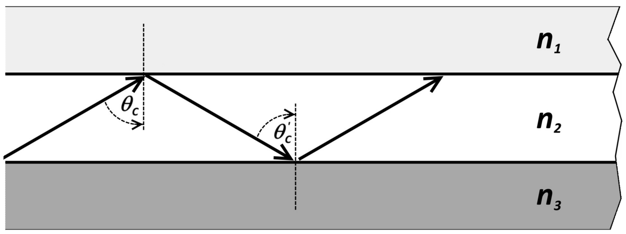

Figure 4: Coupled modes of light traveling in a planar waveguide are totally internally reflected at angles below the critical angles Θ_C and Θ_C' which are unique for the upper and lower interfaces.

Light leakage from the system is reduced when $n_2 >> n_1$, n_3. This condition is met when air is used as the upper clad but a customized low refractive index clad coating was applied underneath the frangible waveguide coatings to enhance their efficiency for Tetramer's applications. Waveguiding through the frangible polymer coatings was achieved at distances up to 8 inches through a 150 µm-thick coating.

3 APPLIED SYSTEMS

3.1 Passive Tamper-Indication Coatings

The high crack density of Tetramer's frangible polymer system provides a useful mechanism for visually indicating tampering events in a passive format. The stored potential energy in the pre-stressed frangible coatings developed by Tetramer can be used to create an amplified response to small intrusion events and presents an attractive platform for tamper-indicating labels, seals, or coatings. As described in section 2.1, any penetration of the material will produce a stress concentration point, triggering the catasrophic franging process. In security terms, there is a large penalty for even small attack vectors used by an adversary attempting to gain access to a volume protected by a pre-stressed frangible polymer coating.

Although the materials are highly stressed, the compressive forces produced at the surface of the coatings provides enhanced hardness and impact resistance, critical requirements for surface coatings. Tetramer has successfully demonstrated the frangible polymers as tamper-indicating coatings on various substrates and has proven their impact resistance and excellent tamper indication properties. These coatings have received interest from the government and commercial leaders in the brand protection industry, and commercialization efforts for these materials are still underway.

3.2 Authentication Tokens

As described in section 2.2, the type of franging pattern in these materials is tailorable and can be used to produce advanced authentication tokens. Tetramer has proposed the design of a Frangible Authentication Challenge Token (FACT™) system wherein multiple layers of transparent frangible films are stacked and loaded into a frame (Figure 5). The frame has integrated, color-coded punches that can puncture each frangible layer individually. This system is designed to operate with an online database wherein the type of frange pattern for each layer is correlated to the color of the punch button based on the processing parameters for each frangible layer in the stack. In the standard use-case, a consumer or supply-chain manager would access the database through a smartphone app, enter the FACT™ serial number, press one of the buttons on the token, and submit an image through the app (similar to current QR code reader apps) and the database would verify the crack pattern associated with that colored button for that specific FACT™ serial number. In order to verify that the database is secure, the app would then prompt the user to press one of the other 4 buttons on the token and presents the stored image for the type of pattern associated with that color button. This allows for both forwards and backwards authentication of the token as well as the database.

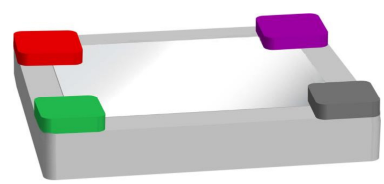

Figure 5: A rendering of the FACT™ system. Approximately 1.5" by 1.5´in size, this small disposable token will generate four unique, pre-defined crack patterns in the center clear window by pressing each of the colored buttons.

The critical advantage of this technology is that the frangible materials used to create each different type of crack pattern are identical in composition, color, and dimensions. This makes reverse engineering of the crack patterns extremely difficult prior to the franging event and provides a significant barrier to spoofing this type of authentication token. Pre-defined shapes such as letters, numbers, or logos may also be designed into the individual layers to add complexity or brand placement opportunities.

3.3 Active Tamper-Indication System

Tetramer has developed LightShield™, an active tamper-indicating system that leverages both the pre-stressed frangible nature and the waveguiding properties of these materials. This system is capable of monitoring the perimeter status of a protected volume in real-time and can be tied to other complimentary tamper-indicating or systems integrity mechanisms for additional functionality.

The LightShield™ system was designed as part of an active-monitoring system (Figure 6.). An integrated LED source (A) is used is used to excite a fluorescent dye (B) within the frangible polymer waveguiding core and across the waveguiding clad layer. The fluorescent emission of the dye is then waveguided through the frangible polymer core across the surface of the protected volume until it reaches the edge of the coating or a pre-defined scattering point (C). Scattering points are configured in the coating just above photodetector (PD) elements in the protected volume (D). The PD elements measure the intensity of the scattered fluorescent dye signal and convert the optical signal to a digital that can be used to monitor the condition of the frangible film. If the frangible coating is penetrated, the optical path for the waveguided light is destroyed or severely obscured, preventing the fluorescent dye signals from reaching the PD element. This drop in optical signal intensity is monitored by the PD element and indicates a failure in coating integrity.

The orthogonal arrangement of the LED/dye and scattering point/PD pairs enables the system to be integrated on numerous platforms without the need for complex light-coupling optics. This system has been demonstrated to be highly effective and is sensitive enough to detect perturbation of the coatings such as the touch of a finger or slight pressure to the surface.

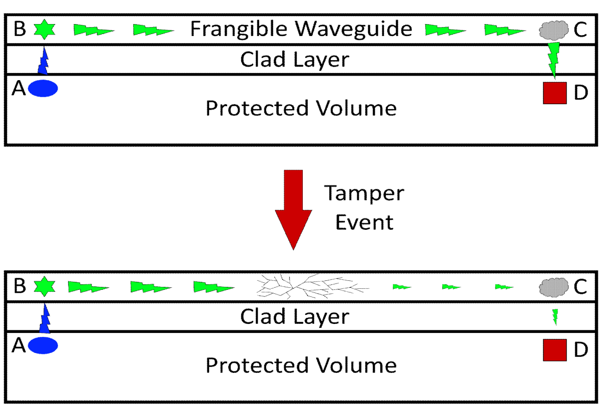

Figure 6: Diagram of the LightShield™ active tamper-indication system developed by Tetramer.

4 COMMERCIALIZATION

Tetramer is actively developing new products with pre-stressed frangible polymer coatings for commercial, government, and military applications. The primary objective of these commercialization efforts is to market a competitively-priced industrial product that will create lift for the higher complexity, higher security products based on these materials. Initial efforts for the tamper-indicating coatings will focus on needs for supply chain and accounting verification within the nuclear industry as well as brand protection applications.

5 CONCLUSIONS

Pre-stressed frangible coatings present a unique material system that has several key advantages for tamper-indicating and authentication applications. The ability to store high levels of potential strain energy in an optically transparent polymer material enables both passive and active tamper-indication products. Additionally, the ability to define the type of frange patterns in a material based on process controls allows robust authentication strategies to be developed around these coatings. These materials present an opportunity to gain a unique advantage over adversaries in the fields of brand protection, supply chain verification, and nuclear security controls.

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