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Editorial

Composite Films for Time Measurement—A Case Study

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Each event starts in the past and proceeds towards the future, going through the present. Time measurement consists in the determination of the length of an event. Over the centuries many types of devices have been developed for time measurement [1]. Examples of primitive technological solutions used for time measurement include hourglass, water clock, candle clock, oil lamp clock, and incense clock, as the most relevant. Today, common types of time measurement tools are mechanical watches/clocks, digital watches/clocks, stopwatches, calendars, etc. Clearly, the measurement of time has always been delegated to mechanical or electrical devices and never to a material capable of slowly but progressively modifying over time its own physical properties, from whose modifications a way to determine the flowing of time follows. However, such a technological solution would not be very difficult to develop by combining knowledge on advanced composite materials and thin-film science. A material capable of self-changing over time and therefore able to act as a clock could be, for example, a resistor with a time-dependent resistance value or an optical filter with a transparency able to change slowly but continuously over a certain time period.

Occasionally pitch has suggested to humans the possibility of being used for time measurement. The 'pitch drop experiment', developed by Thomas Parnell of the University of Queensland in Brisbane (Austalia) in 1927 [2] to demonstrate the liquid nature of bitumen, represents the most famous case of device for time measurement based on pitch (the pitch drips every 7 years); however, further designs for a time related device based on pitch have been proposed too (e.g., the Kelvin's artificial glacier experiment with pitch on a plan, and the pitch flow glacier) [3]. The concept that pitch may be useful for developing a timepiece can be conveniently extended by preparing a pitch-based material capable of gradually and linearly changing its physical characteristics over the time. If, for example, this material changes its electrical conductivity, then an ohmmeter connected to it makes it embody a clock completely different from those fabricated so far. Yet why does pitch suggest this application? The reason is the possibility of inner movement that pitch can offer. In fact, a clock needs movement to work. All non-electric clocks are based on some type of movement: a flowing liquid or a fine powder (sand) is present in a hourglass, oil, wax, and water were present in the primitive clock systems, while an unfolding spring is contained in a more traditional mechanical clock. Therefore, movement is the basic requirement for a material intended for time measurement. Flow is a well-known characteristic of liquids, but it should not be allowed to solid materials. However, there are amorphous solid substances capable of flowing just like liquids do, but they do it very slowly during the time. These substances, modified by fillers, can be used to fabricate composite materials adequate for time measurement, and the resulting devices can be defined as 'molecular clocks', since the flowing of single molecular layers located at pitch-filler interface is the reason for their operation.

Movement happens under the effect of an applied force and this force represents a further requirement for a material devoted to time measurement. The applied force can be simply the gravitational field, or an external force field (e.g., magnetic or electric fields). Materials for time measurement are extremely useful since they can be integrated in the packaging of drugs, food, and electronic items, for example, but at the moment they represent

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a potential that is largely untapped. These materials consist of solids with some physical properties that slowly and progressively (better if also linearly) change over time. Physical properties such as the color, the electrical conductivity, the opacity, the polarizability, etc., can change in an irreversible way over time, and such a behavior can be advantageously exploited for the fabrication of devices for industrial applications such as, for example, the measurement of the shelf life for degradable and rapidly expiring products.

Pitch-metal composites (PMC) represents a new class of functional materials that can be used to develop compact solid-state clocks. Such solid devices, based on a simple self-changing mechanism, can have many technological applications such as chronometers, shelf-life indicators, timers, etc. and be used in a very compact way. The working principle of this novel functional material is the sedimentation phenomenon involving the composite filler in the viscoelastic pitch matrix. In principle, the filler may consist of a metallic powder stable to oxidation like stainless steel or a noble metal (e.g., silver, gold, etc.), but also a semiconductor powder (e.g., germanium, tellurium, etc.), or an electrically conductive ceramic powder (e.g., indium tin oxide, ITO) can be equivalently used. However, metals are the densest materials, and therefore yield the best results for this type of application. Non-toxic noble metals with high density values constitute the ideal composite filler, since these very expensive metals are characterized by extremely high density values (Au: 19.3 g/cm^3, Rh: 20.8 g/cm^3, Pt: 21.4 g/cm^3, Ir: 22.56 g/cm^3). Due to their special shape factor and low density (comparable to that of pitches like colophony), both graphene and carbon nanotubes (CNTs) are not really adequate for the present application. In addition, a segregation process based on floating is less convenient than a segregation based on settling, because forces of lower intensity are involved (the difference between the density of matrix and filler is quite small). With regard to the type of amorphous material to be preferentially used as a matrix, a pitch based on a low-molecular-weight substance, like for example colophony (density: 1.06 g/cm^3) or other tree resins, represents the best technological solution because the viscosity value of these substances is not extremely high like in the case of bitumen, asphalt, and other hydrocarbon-based pitches.

With regard to the preparation of these materials, the blending of the two components can be easily done by increasing the temperature (solution casting is not adequate as fabrication process because amorphous substances hardly release volatile solvents, due to the absence of a segregation phenomenon for these volatile components, since crystallization does not take place). However, a limitation for such a type of device is represented by the strict dependence of viscosity on temperature [4]; consequently, clocks based on this principle require a thermostatic system. On the other hand, these materials can be also used as integral temperature sensor [5] due to the dependence of the measurement time speed (i.e., sedimentation kinetics) on the pitch viscosity, which in turn is related to temperature.

The working mechanism of these devices is very simple: the sedimentation of the dispersed metallic phase (composite filler) by the effect of gravitational force slowly reduces the extension of the region of pitch where particles are embedded. The filler is segregated in a smaller and smaller portion of the sample, thus causing the simultaneous formation in the sample of: (i) an electrically insulating region (with high dielectric strength), completely free from particles, and (ii) a complementary region where the particle concentration progressively increases. In particular, in the last region, the formation of percolation paths can be observed with the flowing of time. However, particles are not uniformly dispersed in this region, but they tend to accumulate near the bottom (i.e., the sample basal plane). In this region, the sample electrical conductivity quickly increases because a network of percolation paths is progressively generated. When the percolation threshold is reached at sample bottom, the electrical properties of this basal surface change from dielectric (insulator) to conductive, and the electrical conductivity value on this face progressively improves to reach a value approximately coincident with the electrical conductivity of the pure metal used as filler. Therefore, the measurement of the sample resistance in the region of the bottom by two interdigitated electrodes does not provide a constant value, but a value linearly growing during the time, and this time-dependent resistance value is useful to fabricate some special type of electric device that can be used as an innovative clock for time flow measurement.

It is possible to develop a very simplified model for the temporal evolution of the composite filling factor. This model does not consider the accumulation of the filler particles at the sample bottom, but it is able to predict the composite filling and electrical conductivity increase. If we consider a uniform dispersion of N identical metal particles, with a spherical shape of radius: R, in a certain volume V° of pitch, having for example the shape of a rectangular prism, then the volume fraction, φ_2, of metal is given by the following equation:

$$\varphi_2 = 4/3\pi R^3 N/(4/3\pi R^3 N + V^{\circ}) \quad (1)$$

As the metallic filler settles at sample bottom, the pitch volume containing the particles reduces and the particles accumulate on the prism basal plane of this reduced volume $V < V^{\circ}$. If we indicate with v the sedimentation velocity of the identical spherical particles, then the volume, V, where particles are dispersed, is given by: $V = V^{\circ} - (S \cdot v \cdot t)$, where S is the surface area of the prism base and t the elapsed time; thus φ_2 becomes:

$$\varphi_2 = 4/3\pi R^3 N/[(4/3\pi R^3 N + V^{\circ}) - (S \cdot v) \cdot t] \quad (2)$$

As visible, the volumetric fraction of metallic phase increases during the time, and therefore the dispersion of electrically conductive particles in the dielectric matrix, initially below the percolation threshold, will gradually concentrate, as time progresses, first up to the percolation threshold and then above it. As a consequence, the electrical behavior of the material in the basal region of the prism changes from dielectric to conductive. This model allows to qualitatively predict the behavior of the material electrical conductivity, which is proportional to φ_2.

The present type of devices is a great example of how a force field (gravitational, magnetic or electric force field) can be conveniently engineered. A timepiece based on the gravitational field could be made by a thin pitch-metal micro-composite layer placed on two interdigitated electrodes. The material must have a percolation composition in order to readily change its electrical conductivity with time flowing. If the device is based on a magnetic field, a neodymium magnet must be placed below the pitch-iron, or pitch-cobalt, or pitch-nickel film.

Thin film and coating technology has a very important role in the area of materials for time measurement. In particular, an ultra-thin layer of percolation composition is strictly necessary for the device fabrication. In fact, if the filling factor, θ, of the pitch-metal composite is taken next to the percolation threshold, then even extremely small variations of θ can cause significant changes in the material electrical conductivity, and this variation typically corresponds to several magnitude orders [6]. Since metal particle sedimentation in pitches is a very slow process, the presence in the composite of a percolation structure could represent a trick to have perceptible variations of the electrical conductivity in short time intervals. A further important consideration is that the percolation structure is first generated in the basal plane of the sample and, with time progress, further percolation structures result in the above planes. As a consequence, an ultra-thin layer can perform the same function as a thicker layer, and consequently this type of device can be conveniently made by an ultra-thin layer deposited on two planar interdigitated electrodes. At beginning the composite composition is uniform inside the layer and it corresponds exactly to the percolation threshold concentration, then with time flowing the above part of the sample will become a better and better electrical insulator, while the remaining part will become more and more electrically conductive. The best place where the sample electrical conductivity can be measured is at the bottom (i.e., the prism basal plane). In addition, a pitch-metal micro-composite is more convenient than a nano-composite for this type of application. In fact, since pitches have an apparently solid nature, it is possible to develop a mathematical model for particle sedimentation, which is based on the kinetic friction force acting at filler-matrix interface. In particular, the acceleration, a, undergone by a spherical particle embedded in the very viscous pitch matrix as a result of the forces acting on it (i.e., weight force, hydrostatic force, and interfacial kinetic friction force) is given by the following approximate Equation (3) (More detail information could be found in the Supplementary Materials).

$$a = g - (3\mu_D \cdot P/d_M) \cdot (1/R) \quad (3)$$

where, g is the gravitational acceleration, P is the atmospheric pressure, μ_D is the coefficient of kinetic friction at interface, R is the particle radius, and d_M is the metal particle density. This equation is quite different from the classical expression for the particle speed, v, derived by comparing the Stokes' law to the resultant of the applied forces. However, this mathematical treatment takes correctly in account of the extremely slow particle movement in pitch. As visible, the sedimentation acceleration approaches the acceleration due to gravity with increasing of the metal density and the particle size, and therefore, a raw powder of a noble metal is the most convenient choice for an electrically conductive filler.

A further important possibility is to control the pitch viscosity by mixing it with polyols [7]. These special formulations may look apparently solid, but have lower viscosity values than the pure resin and such physical characteristics is useful for increasing the rate of sedimentation.

An example of molecular-clock can be a simple time-dependent resistor (TDR), that is a passive electrical device made by a pitch-metal mixture with time-dependent electrical conductivity. This device unendingly increases its conductivity at the bottom surface because of the slow segregation of the electrically conductive filler with high specific weight, dispersed in the pitch (e.g., colophony). Segregation is related to the different density values characterizing the inorganic filler and the organic matrix, and it consists in the slow but progressive settling of the metallic powder at the bottom of the pitch matrix. Consequently, time causes a continuous change in the material electrical conductivity, and consequently it can be used as time flow indicator (i.e., clock). However, due to the optical grade of colophony, the clock can be also based on some optical measurements, for example transparency at the sample bottom should decrease as the effect of the filler segregation.

In conclusion, the process of sedimentation of an electrically conductive micrometric powder in a highly viscous (apparently solid) dielectric matrix can be used to fabricate a composite material capable to spontaneously modify its electrical properties (e.g., electrical conductivity, polarizability, dielectric strength, etc.) over time. Optical properties (e.g., transparency, refractive index, etc.) also change and this variation can be used for the same purpose. Sedimentation may take place by the effect of the gravitational force field or by the effect of an electrical or magnetic field placed near the sample. In this case, the device operation is not dependent on its orientation. Different materials can be used as matrices (e.g., greases, gels, resins, etc.); however, vegetal resins, such as colophony, are the most adequate to achieve an apparently solid material able to self-modify over a large time period. The use of a noble metal powder as electrically conductive filler is very convenient, principally because of the high-density value that characterizes this type of solid. The optimal composition for the composite is that corresponding to the percolation threshold because it allows significant conductivity changes in short time periods. The development of materials for time measurements will launch a completely new research topic in material science, that will require knowledge in the area of films and coatings as the main investigation tool.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings12081118/s1.

Conflicts of Interest: The authors declare no conflict of interest.

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