

Editorial

Looking for New Materials: The Molecular Clocks

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Advanced Functional Nanostructured Films and Coatings for Energy Applications

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Frequently, new materials have been discovered by looking at the interface among some of the already existing material classes. This creative approach has been used, for instance, in the development of nano-sized materials, which are merely an intermediate matter form, located between the molecules and the bulk solids. Similarly, hydrogels are a type of solid phase intermediate between water and polymers, while aerogels are intermediate between gas and ceramics; composites, depending on their filling factors, range from metals to ceramics (metal matrix composites, MMC) or from polymers to ceramics (polymer matrix composites, PMC), etc. Now, between liquids and solids there is the class of the ‘amorphous solids’, which can also be considered as the class of the ‘extremely viscous liquids’. These ‘frontier materials’ can be modified by embedding an adequate functional filler, in order to achieve some technologically useful hybrid, which is adequate for applications based on its time-depending properties.

The ‘flat shape’ of solid matter, commonly referred as film or coating, depending on the presence or less of a substrate, has played a fundamental role in materials science and technology both in the past and in the present. Recently, graphene and other 2D materials (e.g., molybdenum sulfide, MoS₂) have had a huge success because of the large number of physical anomalies that this special shape is able to offer (e.g., optically transparent electrical conductor, zero band-gap semiconductor, high specific surface area adsorber, etc.). Films and coatings are not equivalent solid matter forms. Indeed, coatings is the only organization of matter able to maximize the interactions with the substrate, and such an unique property may offer a variety of applications for coatings, never developed before. This flat shape of matter in the form of thin film or coating is also the only form of matter organization capable of maximizing the interactions with a force field such as, for example, the gravitational field, the electrical field, or the magnetic field. Therefore, the possibility of developing some type of composite material, capable of undergoing the effects of a force field (electrical, magnetic or gravitational) by spontaneously acquiring this kind of shape if placed in it, can be very important. Matter with low cohesion like fluids very commonly show such a behavior (e.g., ferrofluids), but solids, because of their usually high cohesion, do not typically reshape in a force field. However, solids capable of reshaping for the effect of a force field can be developed on the basis of the low-molecular-weight amorphous substances. Such a time-related behavior of this hybrid solid matter can be advantageously exploited for technological applications in different industrial areas.

Depending on the intensity of the cohesion forces (i.e., covalent, ionic, dipole-dipole, or Van der Waals interactions), solids may group in ‘stationary’ and ‘dynamic’ molecular structures. A crystalline solid phase can be considered as a stationary molecular structure (that is, a covalent or ionic or dipole-dipole based framework, which remains structurally unchanged over the time). A completely different situation is that experienced by those amorphous solids (glassy materials), made of small organic/inorganic molecules. Indeed, low-molecular-weight amorphous solids are dynamically evolving molecular structures in a continuously changing structural status. On the other hand, amorphous solids can be alternatively described as very viscous liquids, and their ability to modify the own molecular structure over the time is related to the molecular mobility, which depends on



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the particular viscosity value characterizing these systems. These substances structurally change more slowly with increasing of viscosity, i.e., they are less molecularly active.

This special state of the matter can offer great technological potentialities because it is a kind of 'living matter' capable of self-modifying over the time, and therefore they are able to show something like a 'vitality' that can be conveniently exploited for practical applications, such as, for example, measuring the flow of time. The lifespan of these materials is represented by the time they require to reach the own thermodynamic equilibrium state, where the energy content of the substance has reached its minimum value. An extremely viscous liquid or equivalently a solid that takes the shape of the container is a structurally evolving material, and such slow but continuous change of the molecular structure can be exploited to mark the time just like an hourglass may do. For example, when these solids are used to fill a pipe, they slowly flow through it, and after weeks, months, or years they can even drip away from one end of the pipe. Solid pieces placed on a flat surface tend to spread on the substrate, that is, to become a thin film coating the substrate surface since the minimum energy content corresponds to a thin layer if the interaction with the substrate are favored with respect to the internal ones. Therefore, a film or a thin coating is the ultimate goal of these 'living materials' and their lifespan and molecular activity depends on the strength of the interaction with the substrate. The solid will modify its shape and spread on the substrate, leading to a thin coating layer if the interactions with the substrate are favored (that is, hydrophobic solid on a hydrophobic substrate or hydrophilic solid on a hydrophilic substrate). Otherwise, it will not tend to evolve or to evolve only minimally if the interactions with the substrate are not favored compared to the internal ones. From a theoretical point of view, the resultant among gravity, applied external pressure, adhesion, and surface tension is the driving force for the shape evolution of the 'living' solid; however, from a practical point of view, a gradient of gravity force is not enough to cause a shape evolution for a small piece of an amorphous molecular solid; only liquids for their very low cohesion forces may change shape from the effect of gravitational force. The situation for a macroscopic sample is quite different; a photograph of the solid taken at regular time intervals may show its progressive shape evolution with transformation, for example, from the pseudospherical shape to a thin flat film. However, there are many other more convenient ways to evidence the structural evolution of this material over the time: if the solid is placed on a planar capacitor, the capacity of this electrical devices will evolve during the time. An electrically conductive (but quite resistive) phase, like the graphite powder, can be dispersed in the molten material up to achieve a percolative structure, in order to make the solid an electrical conductor. The electrical measurements performed on this composite solid shows a time dependent resistance value, uniformly and continuously evolving up to the achievement of the equilibrium state. To make a composite material having a magnetic phase (e.g., magnetite) uniformly dispersed in the solid is also an interesting possibility. A magnetic field applied to the solid is able to force the solid to change its shape, and this process can be easily detected by measuring a magnetic property of the solid body. Many other approaches can be used both to induce a change in the shape of the amorphous solid and to detect the shape evolution of the solid. Such 'flowing solids' can be used to fabricate compact clock mechanisms, based on a simple and very effective molecular gear. Different models of time markers can be easily designed by using these 'flowing solids' and be used as switches able to self-activate after a precise time period or above a certain temperature threshold, devices for measuring the material aging or the shelf life in food or drug packaging, etc.

However, such solid materials can be also used simply to visualize force fields, as common ferrofluids already do. The property change will be very sensible if the functional phase uniformly dispersed inside the flowing solid matrix is nano-sized, since very small variations of the embedding matrix can determine much more significant property changes. Therefore, a flowing nanocomposite can be preferred to a simple micro- or macro-composite material. Both amorphous polymeric solids (e.g., silica, organic polymers, etc.) and low molecular weight solids can be potentially used to fabricate these nanocomposite materials,

but flow in high-molecular-weight solids always ends in negligible results for the very scarce mobility of these large molecular chains at room temperature. Differently, low-molecular-weight solids are characterized by moderate molecular mobility, even at room temperature, and consequently they are preferred substances for the present application. On the other hand, mobility in liquids is too high to be used for time flow measurements.

Circles in the tree trunks have been used to measure the time (the age of the plant) and from trees may come the base materials, useful to measure the time (that is, materials with time-related properties). Indeed, the resins of some trees (like fir, pine, etc.) are high viscous liquid phases that, after turpentine removal by distillation, give solid materials, known as colophony, that behave just like a solid with an evolving shape. This substance does not crystallize, but forms amorphous solids because it is a complex mixture of the abietic acid isomers. It is required only to make a blend of this natural substance (colophony) with a conductive or magnetic functional phase, in order to achieve an electrical/magnetic device with some dynamically-evolving physical characteristics.

In conclusion, it is well known that coatings and films are playing a crucial role in the material science field, the technological potentiality of these special solid structures are widely recognized; however, there are many others ways to exploit their potentialities that cannot be even imagined and will be inevitably discovered progressively over the time. Here, as an example, the role of nanostructured films and coatings in a completely new field of material science, that is, the molecular clocks, has been presented as an example of the incredible applicative potential of these types of solid structures. The possibility to develop solids with properties progressively changing over the time is one of the last prospective of material science, which can be exploited, for example, for time measurements. The availability of molecular clocks or also new devices capable to self-activate after a certain time period is always very useful in the industry, and a material with some property that spontaneously and linearly changes over the time represents the ideal situation. However, the property must be easy to measure; a property such as, for example, the electrical conductivity, the electrical capacity, the opacity, or the color could be adequate. However, this property must modify continuously and indefinitely, or at least over a very long period of time. Material combination represents the way to achieve easy-to-measure properties, and such a composite material with some continuously evolving physical characteristics is the basic component for the fabrication of a device for time measurement.

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