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Evolving the Future of Smart Adhesives: Adhesives Utilizing Layers, Composites and Substrates with Smart Materials

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Abstract

The focus of this chapter is to present emerging technologies within the category of smart adhesives which have the potential to grow into a significant industry segment of adhesives, coatings, layers and hybrid chemistry solutions. We will examine the history, evolution and potential direction of materials and techniques that could yield functional and practical smart adhesives of the future.

Keywords: smart adhesive, damping, resonance, nanotube, thermal response

1. Introduction

1.1 Smart adhesives: evolution

As adhesive innovations continue to advance industries can exploit attributes of discrete material discoveries, hybrids and applications in order to create new engineered materials, composites, layers and coatings to strive toward adhesive compounds that are so amazing they appear to be “smart” [1]. It is important to note that these advancements, enhancements and innovations will simply represent the ‘State of the Art’ for a moment in time. We live in an exciting time as advancements are occurring at exponential rates which are bringing many opportunities for rapid innovation through cross-industry solutions. This means that science and technology are rapidly reaching intersections that allow applications to be realized as scalable solutions in size and ease of deployment. Scale can be thought of as macro-, micro- and nano-scaled. Macro may be a component that you hold in your hand such as a washer, gasket or o-ring. Micro may be a mixture of components that are apparent to the naked eye and Nano may be a molecular array, bonding, layering or complementary mating that is smaller than can be seen but can be quite powerful in application value.

1.2 Background adhesive review

Ever since their development, adhesives have been used in every industry for everything from constructing containers to adhering shingles to a roof, and nearly everything in between. Adhesives provide several advantages over other binding

techniques such as sewing, mechanical fastening, etc., including the ability to bind together dissimilar materials, make design choices that would otherwise be unachievable, and more efficiently distribute stresses across a joint, to name a few. However, adhesives also suffer from several disadvantages. Adhesives may experience decreased stability at less than ideal conditions (i.e., at high or low temperatures). Further, the larger the objects, the more difficult it becomes to adhere the objects together if the bonding surface area is small. Finally, where a high degree of adhesion is desirable so that the materials do not become separated, it may be difficult to also provide a sufficient degree of flexibility to allow the materials to expand and contract due to changes in the environment surrounding the adhered objects. As a result, the adhesive, or even the adhered object itself, may malfunction.

Properties of desired adhesive considerations include:

- Bonding
- Thermal
- Durometer
- Viscosity
- Resonance
- Bonding
- Resilience

2. Smart materials: background overview

Smart materials are becoming an important part of our future, and in many cases they are right under (or above) our noses today [1]. Every-day examples range from your child's forehead thermometer to your sunglass frames.

Children's forehead film thermometers are inexpensive and convenient tools for measuring approximate temperatures based on the surface reaction of materials in a layered film. But what makes it "smart"? The particles that are layered and positioned in the thermometer film are specially selected inks and polymer particles that change their reflective properties based on the surface temperature. The resulting effect creates the appearance of intelligence by providing a viewpoint of perspective to the user. The particles are individually performing a specific localized reaction to a stimulus that is fundamental to the particles themselves. In this case the attribute of the particles is that they change their optically reflective properties based on temperature. This gives the user the apparent viewpoint that the film appears to become "smart" by providing a reading of temperature in color and numerical information.

Another smart material example that we use every day is built into most of our sunglass frames through the use of shape memory alloy material. One of the most amazing and spectacular metal alloys in use today is nickel-titanium [2] (also known as Nitinol). One of the properties of this material is the ability to program a shape of the metallic structure under extreme temperatures. This seemingly magical property is commonly called Shape-Memory. The resulting shape can be recalled through material memory by reheating the object to a nominal temperature, which will cause realignment of the particles to the original programmed shape. Other uses for Nitinol alloy is a form of wire called muscle wire. The wire shape can be

formed in such a way that it effectively contracts its length like a muscle when heated. Another principle of the material is that it is electrically conductive.

Therefore the programmable stimulus can be in the form of electrical energy and perform motion based on a computer signal. This is very important for the advancements in robotics and industrial automation.

What is a smart material?

So what is a smart material? The generally accepted definition is, “A material that exhibits one or more properties that can be significantly changed in a controlled fashion by external stimuli” [3]. You could therefore generalize this definition to say that everything and every one of us is a smart material. But, in the context of material science today we focus our definitions to the nonobvious and spectacular.

I want to make this point because the perception of spectacular and common knowledge is an ever-changing spectrum. In the not-too-distant future we will find potential to control molecules in ways that were not previously possible. An example of this is in the ever-expanding discoveries based on DNA and protein modeling of matter [4].

We are all examples of the spectacular nature of smart materials that have been programmed by DNA coding becoming organisms and humans. We are also continually programmed by external stimuli reacting and responding to ever-changing situations. The fact that we gain a greater understanding than we previously had does not make these now-known facts less spectacular.

For example, the most basic discovery of moving particles based on temperature was shown clearly through the invention of the Galileo Thermometer in the 1600s [5]. This was an amazing accomplishment of a physical set of attributes based on object density and fluid-object displacement.

The temperature can be observed by the user in a self-contained temperature acquisition and display device. A truly amazing invention for its time and still respected today. However, we do not think of this as spectacular in today’s high-tech world.

Many scientific discoveries become obsolete over time and industries lose interest in the scientific fundamentals of the inventions and discoveries that once were thought to be magical and spectacular. Another example of a scientific principle that is still widely used today but is becoming obsolete is the principle of bimetal displacement based on temperature. This technology is one of the world’s simplest thermostat inventions (**Figure 1**). The movement of the two different metals occurs due to each metal having different attributes based on temperature. The net effect is a predictable movement of the combined structure of bimetal commonly known as a bimetal strip [6]. You can imagine that the movement of the heated and cooled bimetal shape could be connected to an ON/OFF switch where the switch is pushed upward to turn ON the air conditioner and pushed downward to turn OFF the air conditioner. This is the basic structure of almost all mechanical thermostats made over the last hundred years. One interesting note related to this “magical” phenomenon is that we do not think of this solution as a smart material in today’s modern world.

So, where is the world of discovery heading and what should we look for as significant smart materials for the future?

Areas of accelerated development in smart materials:

- Polymers
- Ceramics
- Carbon forms
- Mixed-mode hybrids.

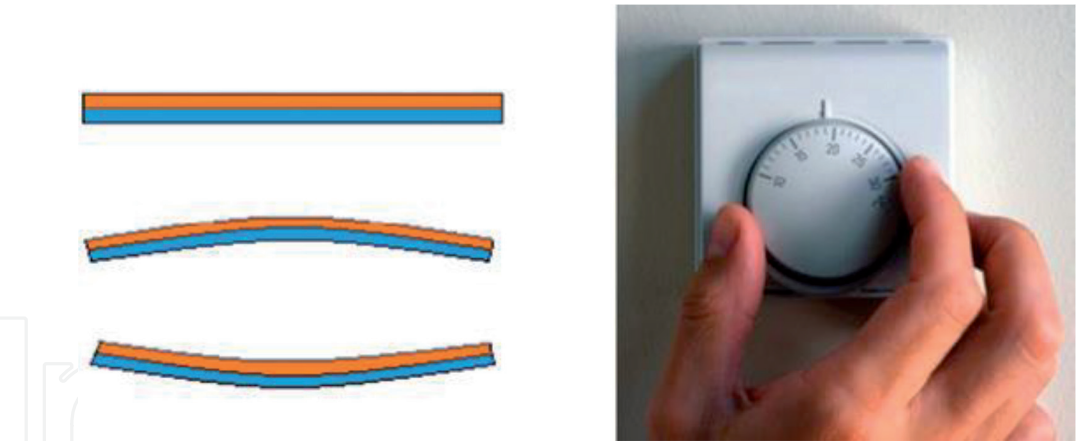


Figure 1.
The principle of bimetal displacement based on temperature (the thermostat), could at one time have been considered “smart” technology. Source: [6].

2.1 Smart materials: details

Polymer chemistry advancements have become part of our everyday lives [1]. The addition of long-chain water soluble polymer lubricant strips have helped in the act and art of shaving by allowing a renewed application of lubrication in every stroke. The apparent structure of the strip is perceived as a magic piece of plastic to most users as they just wet the surface and it continually provides lubrication over hundreds or thousands of shaving strokes (**Figure 2**). The material in the form of polymer molecules forms chains that transfer from the strip to the skin, which provide a smooth surface coating for the razor blades to float over while the cutting surface removes the unwanted hairs, therefore reducing pain during shaving.

Advancements in polymer research have also provided the ability to create specific molecular features or attributes that can be manufactured to provide various states or forms. One type of polymer that can become “smart” utilizes the property of thermochromatic transition states (**Figure 3**). This technology is seen in the previous example of the children’s thermometer film but can also be used to create color changes in items dating back to the mood ring of the 1970s. In today’s world we can utilize these properties to allow polymer particles to become transparent



Figure 2.
Lubricant strips on razors demonstrate polymer chemistry advancements that have become part of our everyday lives. Source: [11].

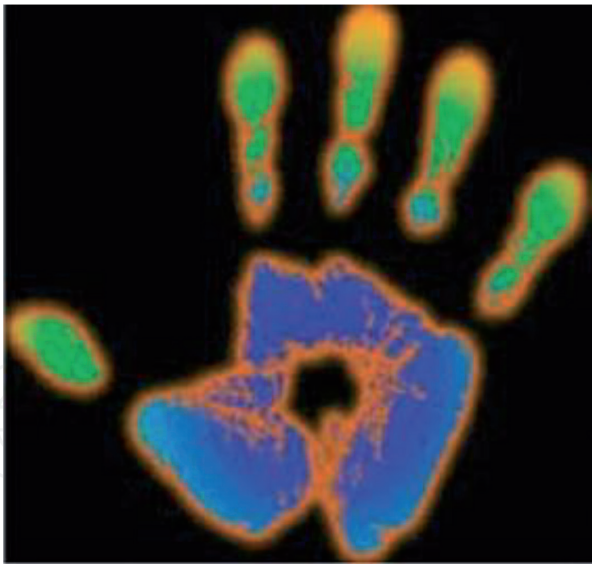


Figure 3.
One type of polymer that can become “smart” utilizes the property of thermochromatic transition states. Source: [1].

based on temperature rise or temperature fall. This can be used to create multilayered signage including building materials that can change color or become invisible.

Another version of smart materials based on temperature is a hybrid material application that utilizes conductive electrical current flow to visually indicate a quantitative energy meter directly on the side of a battery (**Figure 4**).

Thermochromic inks can be used along with a resistive film coating. The display will change based on a battery’s voltage. The energy must be sufficient to create a proportionate current flow through the film in order to generate enough heat to display 100% full. The lower the voltage—the lower the bar graph as seen by the observer. Smart particles provide a power meter with no computer involved. Piezoelectric elements can be formed as films, wafers or crystalline particles that can be used as sensors and that can also become actuators (**Figure 5**). The physical properties of the surface can be energized to move based on the voltage level and polarity of the stimulus provided differentially across the surface of the crystal. This property can be used to make a movement, a beeper or a speaker. Another interesting property of the material is that the inverse operation is possible as well. This means that the same device that is a speaker can also operate as a microphone or a displacement vibration sensor. It can also generate small amounts of energy during vibration to yield energy harvesting.

This brings an interesting property of a device called a Peltier device [7] or thermoelectric cooler. The primary function of the special silicon junction is that you can provide a voltage potential that creates a current flow, and the material attributes create a cooling effect on one side of the device while creating a heating effect on the other side (**Figure 6**). An inverse attribute is that the device can also generate a small amount of energy if you provide a temperature differential with sufficient heat and delta temperatures. This feature can be used as a form of energy



Figure 4.
Smart particles provide a power meter directly on the side of a battery. Source: [11].



Figure 5.
Piezoelectric elements can be formed as films, wafers or crystalline particles that can be used as sensors and that can also become actuators. Source: [1].



Figure 6.
The special silicon junction of the Peltier device can provide a voltage potential that provides a current flow that creates a cooling effect on one side of the device while creating a heating effect on the other side. Source: [1].

harvesting in the presence of differential thermal surfaces. Organic LEDs are providing the ability to provide an electrical stimulus across a junction of material that can create a transmission of light at a specifically programmed wavelength (or color) (**Figure 7**). An interesting part of this material advancement is that the particles can be manipulated in such a way to create a nonplanar or flexible surface. This will likely evolve into silk-screened TV screens and spray-on digital signage as active billboards.

Electronic ink film is an optical memory technology that can be formed as a grid of static programmable electrochromic (SPEC) particles that are less than 100 microns each that can be used to create sensors, flexible signage, labeling and screen displays. One of the unique properties of the SPEC particles is that they can become reflective or light absorbing and remain in that state semi-permanently without the need for power. Electrical signals in the form of pulsed waveforms are used to excite the particles into discretely programmed states of black, white or a variety of colors (**Figure 8**). The display film is flexible and can be reprogrammed down to the pixel



Figure 7.
Organic LEDs can provide an electrical stimulus across a junction of material that can create a transmission of light at a specifically programmed wavelength (or color). Source: [1].

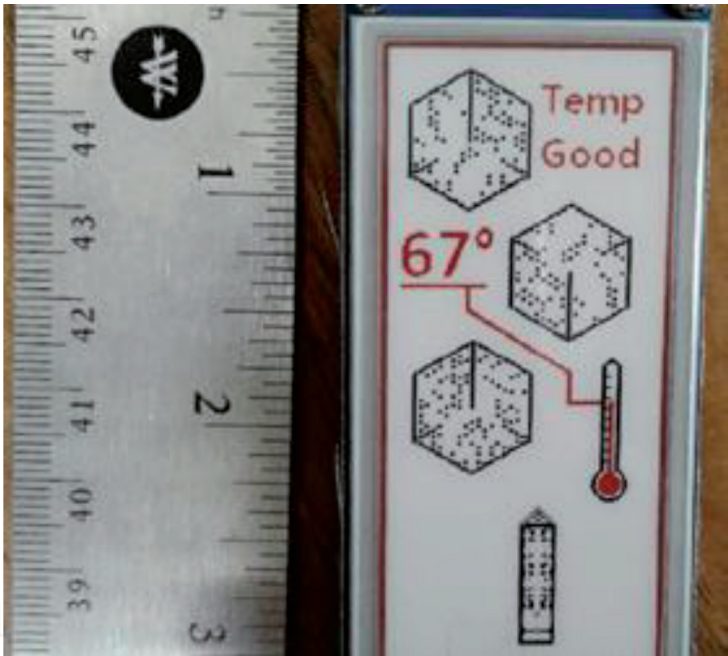


Figure 8.
Optical memory with static programmable electrochromic (SPEC) particles formed as a grid of dots that are less than 100 microns each that can be used to create flexible sensors and nonvolatile labels. Source: [11].

level. There are also segment and block modes for the particles to allow large areas to change colors or thermal properties such as reflective or black body radiating thermal collectors.

Thermochromic polymer particles can be used to coat a surface such as asphalt shingles to allow color changes to the surface-applied particles based on temperature.

Figure 9 shows an example of 90°F trigger programmed particles that reflect light in the summer and turn black in the cooler months in order to absorb heat in the winter. The purpose of the coating is to allow modification to existing production methods while providing a variety of color mixtures and patterns. It is also possible to create other building material solutions using this methodology including inside walls, ceilings and counter surfaces. In some cases the material itself could be injection molded or extruded to provide a functional composite material solution.

The hybridization of these and other smart materials is making its way into other materials such as paints and coatings. One example of this is the recently discovered state of carbon known as graphene, which allows structural enhancements that can be mixed with a carrier component and grown onto a substrate. The end result can form a lattice structure that creates extremely strong bonds structurally as a hexagonal grid. One of the important properties of this material as a lattice is the ability to conduct electricity. This means that the advancements of sensors and computing devices are abundant.

One of the most exciting areas of research into smart materials is in the field of carbon forms such as Fullerene C-60 [8] (Buckyballs), carbon nanotubes (CNT) and graphene.

Figure 10 shows a suspension of CNT that can be used as a coating, paint or adhesive when mixed in production with an appropriate carrier material. Carrier materials such as silicone rubber, epoxies and acrylic paints can provide lattice structures that enhance elasticity, impact resistance and resonant tolerance such as damping properties.

The electrical conductive properties of the carbon additives can create a hybrid material that can be used to create sensors and actuators to tune or de-tune resonant vibrations.

The hybrid composites can also be used to change durometer and response to shock through electrical and/or thermal excitation. Thermal heating modes can create “distributed warming” by conducting an electric current through the hybrid composite to create solutions such as avoiding brittle carrier material characteristics in the cold.

Plastic and epoxy carriers can be formed and molded into strategic shapes based on application or to exploit physical vibration characteristics based on strategically generated waveforms for material displacement. Applications include sound damping and active noise canceling.

Flexible silicone adhesives, gaskets, washers and o-rings can be easily formed to provide programmable response to vibration, pressure, temperature or other electromagnetic properties. Externally powered warming caulk can be created that can offset humidity-based fogging on glass surfaces or defrost cold surfaces.

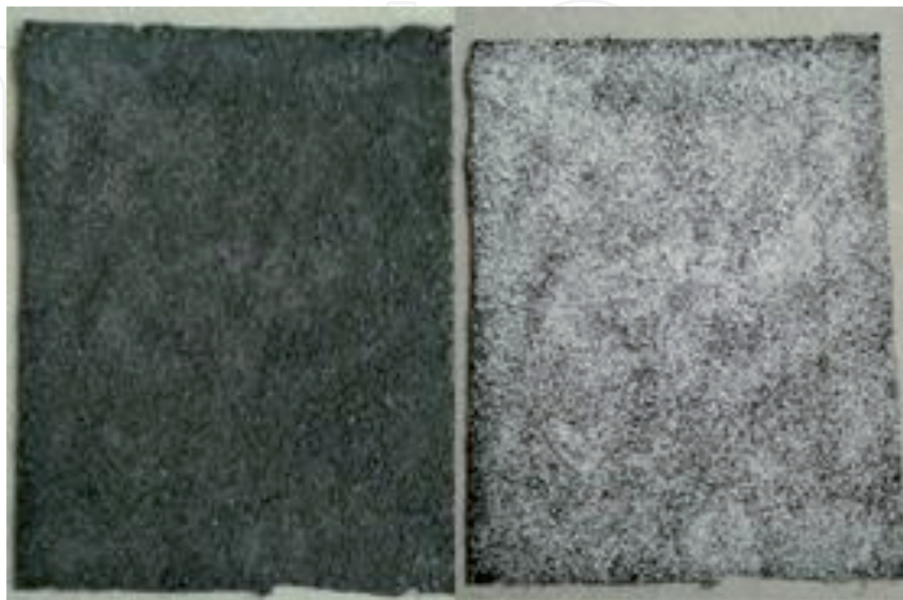


Figure 9. Thermochromic polymer particles can be used to coat a surface such as asphalt shingles to allow color changes to the surface-applied particles based on temperature. Source: [11].



Figure 10.

A suspension of CNT that can be used as a coating, paint or adhesive when mixed in production with an appropriate carrier material. Source: [11].

Carbon nanotubes form a contiguous lattice structure during the curing process of the carrier that provides an evenly distributed electrical network throughout the hybrid composite material. One of the inherent properties of CNT lattice structures is the ability to absorb electrostatic discharges (ESD), which can destroy electronic devices. This makes hybrid composite CNT smart materials attractive as electrical safety improvement solutions. Applications such as CNT coatings and potting compound adhesives can become a solution for thermal dissipation as well as energy discharge surface enhancements. Carbon nanotubes and graphene can be structured together in a lattice formation in a complementary manner that can form electrical sensory networks including the formation of a function field effect transistor (**Figure 11**). With this ability to become a smart material hybrid functioning as a transistor we enter a new frontier of semiconductor research that takes smart materials beyond the perception of spectacular to a true functioning computer circuit within the materials of tomorrow.

2.2 Smart adhesives: feature potential

Smart adhesives will someday allow the sensory monitoring of their attributes in real-time and additionally provide a means for tuning (or de-tuning) the properties toward an ideal operating state [1].

Thermal properties are critical to many applications and temperature can affect many of the other attributes listed above. Therefore, much research and development focus is placed on the ability to sense or observe temperature as an absolute reading or a differential reading between surfaces. Additionally, the controlled response mode is desirable to warm or cool mating surfaces (or the adhesive core itself).

Resonance is another important attribute topic for the reinforcement or prolongation of vibrations by reflection from a surface or by the synchronous vibration of a neighboring object [9]. The ability to absorb vibrations can extend life and avoid failure modes to adjoining components. This functionality can be referred to as damping.

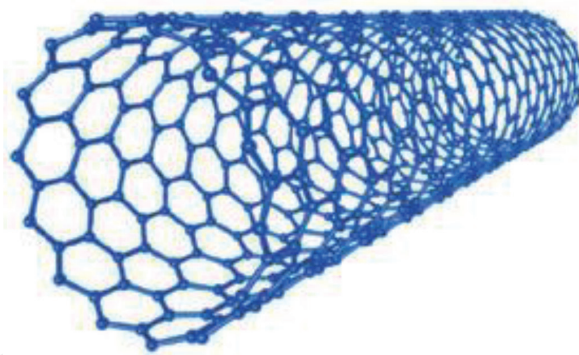


Figure 11.

Carbon nanotubes and graphene can be structured together in a lattice formation in a complementary manner that can form electrical sensory networks. Source: [1].

Damping adhesives have the ability to absorb sound and/or vibrations in such as ways as to isolate the vibrations from one mating surface and attenuate the force seen on the other mating surface. In some applications it may also be desired to absorb or move the vibrational energy throughout the adhesive material itself in order to extend the life of the adhesive structure and bonding properties of the system.

Vibration can be an attribute that is quantified as resonance where energy over a period of time reaches a repeating cyclical pattern that can become destructive (or in some cases can be desirable). The resonant frequency of an object is commonly measured by the number of vibrations per second and can be represented as Hertz. The ability to vary or alter energy cycling is based on measurable components of amplitude, fundamental frequency, frequency harmonics, thermal loss and transfer of vibration known as propagation.

The force experienced by a surface can be transferred into the adhesive's mating surface through layers or composite core material(s) and ultimately propagate onto the adjoining alternate surface. Motions within the adhesive core materials (and layers of the adhesive) will either transfer energy, absorb energy through direct motion or convert the conducted energy into another energy form. The natural form of energy for conversion by default is generally heat. The small amount of heat energy experienced during vibration can create a reduction (or attenuation) of vibrational energy between mating surfaces. Therefore, the addition or removal of heat may be a helpful method of altering the propagated (or conducted) vibrations between surfaces.

The concept of resonance is important beyond the simple idea of vibrating surfaces. Every object or grouping of objects has a specific fundamental frequency of tuned resonance as well as affected responses at harmonic frequencies. Harmonic frequencies are similar to notes on a piano or guitar string. The fundamental frequency is the specific vibration in Hertz that may cause damage to your mating surface components or the adhesive composites themselves. Much like a chord in music having a 1, 3, 5 harmonizing tone, the vibrations will yield other ripples of energy within the adhesive at other frequencies beyond the fundamental tone (or vibration). You can think of this as ripples seen in water as you drop a rock into a lake. The ripple patterns created are more complex than a simple wave of energy.

If the adhesive can absorb certain movements over time it is possible for the peak amplitude of the resonant frequency to be reduced and ultimately smooth out the overall vibrational energy that would cause failure modes to the mating bonded system. The ability to monitor and sense this vibrational energy and allow reduction of amplitude can be a powerful method of extending life to components and bonding attributes. Spreading energy over time and converting vibrational energy to other states are some of the techniques in creating a damping adhesive.

2.3 Damping adhesives

One of the goals of a damping adhesive is the ability to compress and expand layers of material while bonding adjoining surfaces [10]. One method of achieving this goal is to layer or embed components into a carrier where vibrational energy received by the substrate causes particles to compress from a natural expanded state to a compressed state. The composite layer components subsequently return to their expanded state, thereby releasing an opposing energy force onto the substrate which is slightly less than the initial applied energy received by the substrate. The remaining energy loss is in the form of heat through frictional vibrations.

More advanced modes of a damping adhesive system can be realized. A controlled energy field in response to a sensed stimuli can be applied to minimize vibrations. The layered damping system could include a sensory layer which measures an amplitude and frequency spectrum of the disruption. The sensor determines the amplitude and frequency spectrum of the disruption received by the substrate; and the applied force field is dependent on the amplitude and frequency spectrum of the disruption. The overall goal of this composite design is to Tune or Detune resonant frequencies of the overall adhesive bond.

It is also possible to create a vibrational response through thermal or electrical patterns that can provide an opposing force to the energy disruptions by vibrating an opposite (or inverse) waveform to noise-cancel vibrational energy. This is much like the performance and purpose of a sound-canceling headphone effect across two surfaces of adhesive bond layers or substrates.

2.4 Functional overview

Each adhesive serves a particular purpose, whether it be the bonding of metal panels in a Navy ship where the selected adhesive is chosen based on its ability to firmly bind substrates together with a low likelihood of failure in less than ideal condition, or to affix parts of an electronic device together where the selected adhesive is chosen based on its ability to allow the materials to be bonded together but still flex to try to minimize breakage of the component parts. For example, everything composed of matter is in a constant state of fluctuation and has a resonating frequency. If a given object is vibrated at its resonant frequency, or even a harmonic of that frequency, the object may be destroyed as a result of power amplification (i.e., power that is built-up over time at a precise frequency (the object's resonant frequency)). A very small amount of applied energy (i.e., forcing frequency) can thus cause destruction of a large object. Frictional forces (e.g., dampers) may be applied to an object to slow the motion of the resonating frequency and attenuate the amplification. Because adhesive is found in nearly every product, it may be an ideal substance to act as a damper. Indeed, the elastic nature of certain types of adhesives may, by themselves, act as a damper. However, the damping effects of the adhesive may be limited by the characteristics of the adhesive itself. Accordingly, an adhesive that has an increased ability to act as a damper in addition to an adherent is desirable.

A substrate may experience a physical shock, which may have detrimental effects. While an adhesive having flexible properties may be effective to reduce some of the effects of the shock, the adhesive may have limited flexible behavior and over time may begin to fail, becoming more brittle and therefore less able to deflect or dampen the shock such that the substrate remains undamaged. Accordingly, an adhesive having an increased ability to deflect or dampen a physical shock received by a substrate in addition to acting as an adherent could be helpful.

For example, an adhesive with a vibrational damping particles, for reducing the effect of energy transfer to or through one or more of the substrates to which the

adhesive is applied. Damping particles could include particles of different sizes and shapes, and may include nano-particles, micro-particles and macro-particles. In some cases the damping adhesive material may consist of a combination of multiple types of coordinating adhesives which may be strategically selected and provided as a layered medium (e.g., silicone, polyurethane, epoxy, latex, etc.).

Damping particles could potentially contain spokes and may be formed from a material exhibiting superior flexibility and elasticity, such as thermoplastic polyurethanes (e.g., TPU 92A-1). Thermoplastic urethanes may exhibit durable elasticity, high resistance to dynamic loading, high abrasive resistance, quick response and good temperature range. Alternately they may be formed of a material that exhibits greater stiffness than the spokes and optionally interact with elements that may be formed of a material that exhibits less stiffness than the spokes. It may also be desirable to include particles that are magnetic such as iron/steel filings or ferrofluid. The goal of the varying durometer and ingredient layers is to provide a mechanism for monitoring internal forces and optionally apply dynamically controlled responses.

Some of the damping particle materials may be used to form bonds that have a tendency to remain in a naturally expanded state. When a change in the environment of the bonded substrates occurs, e.g., due to an applied energy on the substrate(s) from any direction, the applied energy causes the bonded structure to temporarily flex or compress. As a result of the compression of the structures, some of the stress to the substrates is diffused from the substrate and transferred to the structures. The structures may eventually return to their natural expanded state, and in doing so, return an opposing applied energy to the substrate(s). The opposing applied energy returned to the substrate may be less than the original applied energy. However, due to the structures' ability to diffuse some of the applied energy from the substrate, the substrate may remain relatively undisturbed.

The amount of compression experienced by the structures may be directly related to the strength of the applied energy upon the substrate. The applied energy could be the result of any type of disturbance to the environment, including but not limited to sound waves, electromagnetic waves, seismic waves, changes in temperature and/or pressure, physical shocks, etc. In the instance of a physical shock, the applied energy received by the substrate, and thus the structures, may be substantially greater than the applied energy received as a result of sound waves. Therefore, the bonded structures may experience a greater degree of compression in order to diffuse the energy from a physical shock than they would to diffuse the energy from sound waves.

For example, a smart adhesive may be used for applying ceramic shingles to the roof of a building. The adhesive may be applied to the underside of the shingles and the shingles applied to the roof. During a thunderstorm, the roof may experience hail, which exerts an applied energy on the shingles which, in some instances, may be sufficient that the ceramic shingles would traditionally crack. However, due to the enhanced adhesive having damping adhesive, when the shingles receive an applied energy from the hail, energy is at least partially transferred to the bonding structures such that the structures flex or compress. In this case, because the energy may be greater, the structures may experience a greater amount of compression. The structures then return to their natural state due to the elasticity of the structures, which returns an opposing applied energy to the shingle. Having diffused some of the original applied energy, the opposing applied energy that is returned to the shingle is less than the original applied energy. Accordingly, due to the transfer of energy to the structure, the shingle is less likely to crack.

In another example, a damping adhesive bonding structure may be applied around the outer perimeter of a window. Sound waves traveling through the air hit the window (e.g., on an outside surface), and traditionally would travel through

the window to the other side (e.g., an inside surface). However, due to the damping adhesive, when the window receives energy from sound waves, the energy is at least partially transferred to the damping bonding structures. In this case, because the energy may be relatively small, the structures may only experience a slight degree of flex or compression. The structures then return to their natural state, thus returning an opposing applied energy to the window. Having diffused some of the original applied energy, the opposing applied energy that is returned to the window is less than the original applied energy. As a result of the diffusion of energy by the structures, the sound waves traveling through the window may be considerably decreased.

Damping particle bonding structures can be partially constructed utilizing embedded damping particles with adhesive carriers that take the form of a spheroidal molecule, geodesic dome or other three dimensional shapes. Many such particles exist in nature, or have previously been developed, for various applications. Fullerenes are one example of a damping particle. Fullerenes are a class of allotropes of carbon which are essentially sheets of graphene which can be rolled into tubes or sphere. One example of a fullerene molecule, C_{60} , comprises 60 carbon atoms arranged as 20 hexagons and 12 pentagons to form a soccer ball (or buckyball) shaped structure. Graphene, for example, may be also be provided as a box-shaped structure (e.g., as a layered structure). Carbon nanotubes can be used also where the graphene molecules have been rolled into a 3 dimensional tube. A suspension of tubes in an adhesive may preferably result in the nanotubes being dispersed in various orientations, e.g., some oriented vertically, some oriented horizontally, and some oriented at various angles. In this way, the nanotubes may be effective to dampen applied energy received by any substrate at any angle.

A dendrimer is another example of a damping particle. Dendrimers are spherical polymeric materials whose properties are usually determined by functional groups appearing on the molecular surface. Dendrimers may be used in the synthesis of monodisperse (i.e., uniform) metallic particles. Poly(amidoamine) dendrimers are often used, and the end result may be a dendrimer-encapsulated particle.

The spheroidal, geodesic dome may function substantially similarly where, in the case of C_{60} , the bonds between carbon atoms may have some degree of flexibility which allows the molecule to flex or compress when energy is applied to the molecule.

It is also possible to exploit opposing forces for damping by means of magnetism. It may be preferable for the damping particles to exhibit magnetic properties. In these cases the extended benefit of electro-magnetism may allow damping adhesive response through modes that are electrically or electromagnetically active. When suspended in an adhesive, the adhesive may take the form of a ferrofluid or a liquid (liquid, gel, etc.) that becomes magnetized in the presence of a magnetic field. Ferrofluidic adhesives allow for passive and/or dynamic response to applied energy to a substrate.

Ferrofluid is a unique material that acts like a magnetic solid and like a liquid. In this case, by incorporating damping bonding structures having magnetic properties into an adhesive, the adhesive may be transformed into a ferrofluid. A ferrofluid is superparamagnetic, allowing the liquid to display magnetic tendencies only in the presence of a magnet. Thus, in order to transform an adhesive from a liquid to a ferrofluid, the damping apparatus must have magnetic properties.

Carbon-based particle structures, such as C_{60} , may be naturally paramagnetic, i.e., behaves like magnets in the presence of a magnetic field. Other structures, such as those manufactured from a polymer, may be coated in, or otherwise incorporate a magnetic material such as iron oxide. It may be desirable for the magnetic material to be coated in a surfactant to keep the magnetic structures from sticking together.

Absent a magnet, the particle structures may function as described above. In other words, without a magnet, the damping apparatus may simply compress as a result of an applied energy, thus diffusing some of the applied energy away from the substrate. In the presence of a magnetic (or electric) field, however, the adhesive may become an even more effective damper.

A magnetic field (e.g., using a magnet or a magnetizable material, such as a small rod of iron alloy wrapped in a current-carrying coil) may be applied evenly at or near the areas of the substrate having the adhesive to influence the orientation of the damping apparatus. This may be most useful in the case of an adhesive suspension comprising tubes. For example, if an applied energy most frequently occurs in a single direction across the substrates, then the magnetic field may be applied such that the tubes are oriented so as to transversely receive the applied energy.

An applied energy field may additionally be received by the substrate in one or more concentrated areas. In this case, a magnetic field may be activated only in the concentrated area(s) receiving the applied energy. Thus, multiple pieces of magnetizable material may be provided at or near the adhesive areas such that multiple magnetic fields may optionally be applied. The magnetic damping particles will thus be drawn to the magnetic field(s). An increased concentration of the flexible damping adhesive substrate may thus provide increased flexibility in the area of the magnetic fields.

The magnetic field may be turned on, or off, but the magnetic field may not vary, for example, over time, or in response to dynamic changes in the substrate environment. This method can be accomplished through high-frequency modulation techniques.

As an applied energy, or force energy, is encountered by the substrate, the sensors analyze the applied energy to ascertain the amplitude and frequency spectrum of the applied energy. A force field may be applied at or near the adhesive having damping apparatus dispersed therein to alter the properties of the damping apparatus (e.g., change in orientation, elasticity, etc. of the damping apparatus) in such a way that the damping apparatus experiences a degree of physical displacement at controlled timing intervals based on the frequency spectrum of the applied energy. As an example, the damping particles may actually experience controlled oscillations (e.g., physical displacement along a particular distance). The controlled response of the damping apparatus may result in a response force that is in a spread spectrum inverse waveform which may geometrically stabilize the substrate to avoid peak resonant frequencies which may damage the substrate(s). In other words, the controlled adjustments and corresponding response of the damping apparatus may result in a decrease of the amplitude of the applied energy by spreading the applied energy out over time.

For example, one or more sensors may be placed at or near a substrate (e.g., a window) for detecting sound waves. During peak hours of the day (e.g., high traffic times) the sensors may register higher decibels of sound waves being transmitted and received by the window; conversely, during the evening hours, the sensors may register lower decibels of sound waves. In response, the amount of current pushed to the magnetizable materials may be greater during the day in order to block out unwanted noise than that required during the night.

In another example, a sensor may detect the natural resonance frequency of the substrate. A second sensor (or the same sensor) may detect the frequency of applied energy upon the substrate. If the second sensor detects that the frequency of the applied energy is the same as the natural resonant frequency of the substrate, a magnetic field may be applied (or removed, as the case may be) at or near the adhesive in order to alter the properties of the damping apparatus such that the apparatus may dampen (or alter) the frequency and amplitude of the applied

energy as received by the substrate in order to avoid power amplification and possible destruction of the substrate (or structure attached to the substrate). This ability to tune and detune the damping apparatus in real-time in response to a sensed frequency of a substrate or energy applied to a substrate may allow for supremely customizable products onto which the inventive adhesive is applied. It is important to note that the resonant frequency of the substrate may be altered (or change) by the mass or a surface which may be affixed to the adhesive or substrate.

Applying an electric field (e.g., low voltage pulses) at or near the adhesive substrate to influence the damping structure can allow provide a change in the apparent viscosity or the durometer of the adhesive material. An electric field may be applied at or near the adhesive area. For example, conducting plates may be provided parallel to each other (e.g., at each substrate surface). A voltage may be maintained between the plates by passing current through the plates. The apparent change in the viscosity of the adhesive may be directly dependent on the strength of the applied electric field. Thus, as the strength of the applied electric field is increased and/or decreased, the consistency of the adhesive may transition from that of a liquid to a gel, and vice versa (or to and from a more elastic gel to a less elastic gel).

The change in viscosity or durometer of a material may occur over very small time increments, e.g., milliseconds, making the electrorheological adhesive especially useful in conjunction with sensors. For example, the electrorheological adhesive may be applied to a window. The conducting plates may optionally be opposing sides of the sash, if the sash is constructed of, for example, aluminum. Alternately, conducting plates may be provided parallel to each other on either side of the sash. The window pane(s) may be placed between the plates. One or more sensors may be placed at or near the window pane(s) to measure applied energy to the window pane(s). If the sensor senses an applied energy over a threshold value, the sensor may transmit a signal to cause an electric field to be applied to the plates. In response, the adhesive (via the damping apparatus) may become stiffer in order to reduce the effects of the applied energy.

The damping particles may also take the form of piezoelectric particles. In response to an applied force, the piezo particles become deformed. For example, when the piezo particles are deformed in one direction due to an applied force, a force field (e.g., voltage impulse) is activated (e.g., via a signal from a sensor) to send electric power to the piezo particles to bend in the other direction. In this way, the response of the piezo particles can help to reduce the disruption to the substrate.

Variations of arrangements including combinations of hybrid configurations of smart-materials such as nickel titanium or nitinol can be combined to perform dynamic response by utilizing the properties of shape-memory alloys (SMAs). SMAs and other smart-materials may exhibit properties that allow the molecular alignment to change in physical state (i.e., relative molecular position) based on variations in energy levels experienced by the SMA material. For example, in the form of a wire strand, nitinol varies in length based on the temperature of the SMA itself. In the case of conductive smart-materials such as nitinol, an electric current can be induced into the smart-material/SMA in order to alter the temperature of the SMA-causing the length of the wire to vary based on changes in the wattage dissipated across the SMA wire within the adhesive structure.

Variations of state, position and structure within SMAs and smart-materials can be exploited to embed SMA wires, pellets or thin-film strips within the adhesive structure. By varying the SMA's density, position and relative placement between companion particles the effective resonant mode of the adhesive can be changed based on external stimulus as a controlled response to achieve anti-resonant damping.

SMA pellets can be dispersed within a mixture of particles to create a layer which may have various properties (e.g., fluid, gel, plasma, etc.) that can be altered

in dimension based on externally induced waveforms. A layer may be strategically positioned between two other layers of, for example, pressure sensitive adhesive, which may be equipped with conductive strips or foil plates. Direct contact of the external response waveforms or force fields can be conductive as direct current (DC) or low-frequency. Indirect induced waveforms can also be used to capacitively couple electrical energy through the SMA pellets using strategically selected high-frequency alternating current (AC) waveforms which do not require direct electrical contact. One example of an indirect method of induced waveforms is the use of ultra-high-frequencies that are electromagnetically propagated in the form of short-burst pulse streams that are strategically shaped in amplitude, wave shape and frequency to achieve selective resonance of specific particle layers or positions of particle regions along or within a substrate layer. The short-burst pulse streams are managed over time in frequency bursts where the frequencies are generated in alignment with wavelengths and fractional wavelength timings (such as quarter-wave, half-wave and full-wave periods). These methods can be used to achieve selective areas of resonant tuning (and detuning) in order to vary the durometer of the adhesive layer(s) in real time. In other words, a nearby field of energy can be utilized to vary the anti-resonant damping mode of the adhesive without any direct contact to the adhesive itself.

Damping adhesives may be extruded, for example, and may have a muscle wire (or SMA wire) located within the extrusion. Electric current may be conducted through the wire via contact leads.

Smart-materials can be somewhat slow to respond due to the thermal mass or other physical properties that can slow response time. This means that there is a limit to the response time (or frequency) of the molecular changes in the smart-material (or SMA) itself. One method of obtaining increased performance is to utilize a harmonic frequency byproduct (based on the changes in the physical properties of the SMA material) to assist in the anti-resonant damping process. For example, a change in SMA structure may be possible in 100's of milliseconds occurring in a repetitive pattern at a fundamental frequency (or rate of change) altering the SMA structural alignment. A resonant byproduct of this movement-pattern can be realized by strategically using the 3rd (or 5th, etc.) harmonic with notable energy that can be used to assist in the anti-resonant tuning and detuning of the adhesive structure for damping. By utilizing a higher frequency harmonic as the controlled response damping, you can achieve this result by providing a much lower rate of change to the molecular smart-material/SMA and achieve higher frequency movements in the substrate structure for damping. The net result allows slow movements within the adhesive structure to provide damping to higher frequency vibrations which in turn enhance damping performance of the adhesive.

2.5 Smart conformal coatings

Adhesives, which may be configured as curable coatings which lose tackiness upon curing, have been used as coatings to protect and isolate surfaces of objects. Moreover, adhesives have traditionally not been equipped with means for providing real-time information about the objects to which the adhesives are adhered. Once the adhesive is applied, it is forgotten about, and further information regarding the objects may be determined using other means.

A smart adhesive having damping properties could be used as a conformal protection coating and sensory material health monitoring surface. A damping system for reducing the effects on a substrate caused by a disruption in the substrate environment could include an adhesive having a damping particles dispersed therein. The particles could be configured to provide a controlled response to an

applied force field. The conformal coating system includes a sensor which measures an amplitude and frequency spectrum of the disruption. The sensor determines the amplitude and frequency spectrum of the disruption received by the substrate; and the applied force field is dependent on the amplitude and frequency spectrum of the disruption.

2.5.1 Conformal coating example overview

Adhesive applications may sometimes take the form of a coating, such as a paint or lacquer, although coatings may be any covering that is applied to the surface of an object. Coatings may be used on many different objects to provide benefits thereto. A damping and/or information-transmitting coating may be particularly useful at locations that are relatively difficult for a person to access. One example of such a location, or rather a plurality of locations, is at a pipeline.

A smart pipe coating utilized to adhere sections of pipe together, to locate possible weak spots in the pipe, locate electrically-exposed areas of the pipe, locate ruptures in the pipe and/or provide enhanced communication capabilities along the length of the pipe. One or more pipe sections adhered together at a point of abutment. Generally, the pipe sections may include a machined end designed to fit inside the other pipe section.

Occasionally, the pipe sections are coated with a substance designed to prevent or slow corrosion of the pipes. The coating is designed to prevent moisture in the ground from coming into direct contact with the pipes. Usually, the coating process is completed before the pipe sections are delivered to the construction site. However, the coating is not applied to the ends of the pipes in order that the coating does not interfere with the welding of the pipe sections. Once the pipe sections are welded together, a coating crew coats the remaining portion of the pipe in the coating, and the pipe is lowered into a prepared trench.

The coatings currently available are one-dimensional in that they are designed only to protect the pipes, but do not serve additional functions such as preventing unwanted vibrations, helping to locate potential weak spots in the pipes, identifying locations of ruptures, or increasing communications along the length of the pipe.

A smart adhesive coating could be used as a coating for a pipeline. The coating composition may include bonding particle structures or particles for reducing the effect of energy transfer to or through a pipe. The ability of the bonding particle structures to resist or reduce energy transfer through the pipe as a result of forces acting upon the pipe from both the inside and the outside of the pipe may help to extend the life of the pipe. Programmable sections of the pipeline may be selected to allow variable conductivity from an excitation source onto a desired pipe section in order to provide dynamic cathodic protection (DCP).

The bonding smart particles may be magnetic, and/or electrically or electromagnetically active. The coating may therefore be configured to provide a dynamic response to a force happening upon the pipe. Sensors may be utilized to measure the amplitude, frequency and wave shape of the waveform of the force happening upon the pipe. The sensors may additionally measure environmental attributes, such as soil content (e.g., alkalinity, salinity, temperature, pressure, etc.). Using magnets, electromagnets, electrical pulses, etc., the particles may be persuaded into a position, pattern or oscillation. The persuasion or oscillation of the particles may attenuate the waveform, or present an alternative waveform. The alternative waveform may be inverse to the waveform of the force happening upon the pipe. DCP techniques may be incorporated to prevent corrosion of pipe sections by forming a closed-loop of sensory and dynamic controlled response to provide a superior form of cathodic protection to existing passive (or fixed mode) techniques.

2.6 Smart adhesive research focus

2.6.1 Carrier and subcarrier hybrids

Direct specific research areas have been focused on smart damping adhesive (SDA) applications as gaskets, o-rings seals, caulks and conformal coatings [10]. One of the important concepts in creating a practical smart adhesive solution is the concept of layering films, sprays or laminate surfaces to build-up a composite solution as a smart adhesive. **Figure 12** shows an SDA pad that can thermally warm two surfaces and monitor strain between the two surfaces.

Smart adhesive layer attributes include:

- Bonding properties
- Optical filtering
- Electrical conduction
- Electrical insulation
- Vibrational damping
- Thermal dissipation
- Thermal insulation
- Durometer variations
- Viscosity variations
- Shape memory
- Transducer functions

Research with layers in silicone as a planar sheet, film and spray have shown test data that can provide electrical properties as follows:



Figure 12.
Smart damping adhesives can be formed as pads, gaskets, seals, o-rings or other three dimensional shapes.
Source: [11].

Note: utilizing various mixtures of room temperature vulcanizing (RTV) silicone with carbon nanotubes the following conductivity was achieved:

Electrical layer properties (Ohms per square):

- 1 Meg Ohm for electrostatic discharge layer
- 10–20 K Ohm for pressure/strain-gauge displacement layer
- 10 Meg Ohm for optical transparency layer
- 50–2000 Ohm for thermal excitation layer

Another important topic is the ratio mixtures for a carrier adhesive component such as Silicone (or Epoxy) is the percentage addition of sub-carrier materials such as carbon nanotube or graphene. Note: The mixing methods are currently experimental and meant to establish proof of concept for each layer.

Other carrier components include piezo particle layers for vibrational sensing, controlled frequency response and energy harvesting. Future research will incorporate embedding subcarriers of piezo particles into silicone, epoxy and plastics such as mylar.

The resulting research test gaskets, o-rings and sprays exhibit consistent results and should have a promising future potential in the world of smart adhesives.

Industries have many potential strengths to embrace by utilizing the future benefits of smart adhesives in the future.

3. Conclusion

3.1 Smart adhesives summary

Smart Adhesives have the potential to grow into a significant industry segment of Adhesives, Coatings, bonding agents, layers and hybrid chemistry solutions that do not yet exist today. In the future it is possible that we will achieve layered adhesive solutions that can sense, monitor, communicate, and potentially self-heal. There are many uses of thermal, electrical and physical displacement that will become features in adhesives that will extend the life and functionality of the mating objects as well as the adhesive itself.

The advancements in microencapsulation, film layering, polymer research and hybrid material matrix design is moving exponentially and will likely be a part of your future.

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