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SMART MATERIALS: POLYMERS

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Abstract

Smart materials are those that change one or more of their properties (shape, color, size, etc.) when subjected to an external change in environment. These materials possess adaptive capabilities and perform better than ordinary, dumb materials. They are considered smart because their in-built sensing and actuation capability. Modern products increasingly use them. There are many products on them out of which this paper provides details of 'polymers'.

I. Introduction

The idea of smart materials originated in mid-1980s. The need for new generation of advanced materials in modern applications has led to the development of the smart materials. Their perception implies an ability to be clever, active, and sophisticated. Smart materials are unique in that they exhibit different properties when there is change in their environment. They react to changes in temperature, stress, moisture, pressure, light, electric or magnetic field. This peculiar property makes them useful for certain applications. Their degree of smartness is dictated by their responsiveness to environmental stimuli. They have several advantages over conventional materials. These include lighter weight, no corrosion, and increase in lifespan of the structures that use them. They have an active role to play in shaping our world, whether in designing clothes, infrastructure, cars or airplanes.

Smart polymers are high-performance polymers that change according to the environment they are in. Such materials can be sensitive to a number of factors, such as temperature, humidity, chemical compounds, the wavelength or intensity of light or an electrical or magnetic field and can respond in various ways. Smart polymers respond to changes in environment with change in conductivity, permeability etc.

II. History

Smart polymers were first found in the form of hydrogels. Hydrogels are cross-linked polymers with at least of its monomers soluble in water. The first smart polymer was the PN-iPAAm (N-isopropylacrilamid), which is a temperature-sensitive material. It swells and contracts in a small temperature change.In the 1940s, Flory and Huggins both independently produced similar theoretical expectations for polymer in solution with varying temperature.

The effects of external stimuli on particular polymers were investigated in the 1960s by Heskins and Guillet which are now known as thermo-responsive materials.

III. Types of Smart Polymers

The main subtypes of smart polymers are as follows.

1. Shape memory polymer.
2. PH sensitive polymers.
3. Temperature responsive polymers.
4. Smart inorganic polymers.
5. Electro active polymers.

IV. Overview

1. Shape Memory Polymer-Shape-memory polymers are stimuli-responsive materials.Shape-memory polymers are a class of mechanically active polymers that are able to change shape in response to a stimulus.Shape-memory polymers are a class of mechanically active polymers that are able to change shape in response to a stimulus. They "memorize" a permanent or original shape, undergo deformation to store a temporary shape, and then return to their original "memorized" shape upon exposure to a stimulus. A change in shape initiated by a change in temperature is called thermally induced shape-memory effect. The shape-memory effect results from the polymer's structure in combination with a certain processing and programming technology... A variety of stimuli may be used for actuation, such as heat, infrared or visible light, solvents, magnetic fields, current, and mechanical force. The classic one-way shape-memory cycle has three parts: (1) "programming," which is the stage when the shape-memory polymer is deformed from its original state into its temporary shape using a mechanical force often at an elevated temperature; (2) "storage," which is the stage when the temporary shape is locked by cooling below the activation temperature and removal of the mechanical force; and (3) "recovery," which is the stage when the shape-memory polymer recovers or attempts to recover its original shape.

Applications for shape-memory polymers exist in almost any area of daily life, some are

1. Self-repairing auto bodies
2. kitchen utensils,
3. Airplanes
4. Satellites
5. Intelligent packing

6. Switches
7. Sensors
8. Smart structures
9. Multi-functional surfaces.

Only a few of these applications have been industrially realized to date, because only a few shape-memory polymers have been investigated and even fewer are available on the market so far.

2. PH sensitive polymer: Cationic polymers with amino groups have higher water solubility at acidic pH than at neutral pH. These polymers with pH-responsive dissolution characteristics are widely employed for taste-masking formulations of drugs, which have unpleasant qualities such as bitterness, sourness, saltiness or causing oral numbness. Through suppressing drug release in the oral cavity, taste-masking formulations can prevent the unpleasant tastes of drugs as the polymers are insoluble at higher pH. While being more soluble at lower pH, pH-sensitive polymers can release the drugs in the stomach or intestine for drug absorption or therapeutic purposes at the released sites. The pH difference between the oral cavity (pH 5.8 – 7.4) and the stomach (pH 1 – 3.5) is thus commonly exploited by pH-responsive polymers to control drug release. For example, aminoalkyl methacrylate copolymer (Eudragit E) is a Food and Drug Administration (FDA)-approved cationic polymer having high solubility below pH 5. Microspheres of Eudragit E containing sumatriptan succinate or donepezil hydrochloride have been prepared by spray-drying technique. The microspheres have been shown to be capable of suppressing drug release in phosphate buffer at pH 7.4 or simulated salivary fluid for 1 minute, thus masking the bitter tastes of the drugs. In acidic buffer, both formulations demonstrated immediate drug release and showed plasma concentration–time profiles similar to those of marketed products. Moreover, faster drug release at acidic pH than at neutral pH has been observed with pellets containing quinine sulphate and granules containing promethazine prepared using Eudragit E. Coating of Eudragit E on particles containing atorvastatin for oral disintegrating tablets has also been reported. Further, slow drug release, low absorption of drug or absence of therapeutic effect could be the risks for patients with achlorhydria or dosed under fed condition. Polyvinylacetal diethylaminoacetate (AEA) is another cationic polymer used in pharmaceutical industry for pH-dependent drug release. AEA has been reported to be insoluble above pH 5.8. Microspheres of AEA containing trimebutine maleate have been prepared by a water-in-oil-in-water (w/o/w) emulsion solvent evaporation method .The

microspheres suppressed drug release at pH 6.8 but immediately released drug at pH 1.2. AEA was coated on sildenafil (Sdn)–montmorillonite (MMT) Nano hybrid for taste-masking. The cationic Sdn molecules were intercalated to MMT, an inorganic clay material. The strong interaction between Sdn and MMT prevented drug release at both pH 1.2 and 7.0. While the release of Sdn in simulated salivary fluid was suppressed by an AEA coating on Sdn–MMT, DE intercalationof the drug from MMT at acidic pH could be achieved due to the protonation of AEA; therefore, Sdn could be promptly released in the acidic stomach environment. Plasma concentration–time profile of this system has been reported to be similar to those of marketed products in beagle dogs. The two polymers described above are the only FDA-approved cationic polymers; however, combination of the polymers and other components might result in more specific response to gastric pH and better controlled drug release in the oral cavity and stomach.

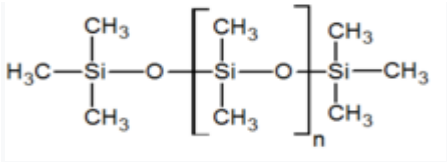
3. Temperature responsive polymers: Thermo-responsive polymers are the most comprehensively studied responsive polymers because of their unique property of sol–gel transition above certain temperature. Some of them also show phase transition near to physiological human body temperature. Moreover, these polymers can be modified to show sol–gel transition at desired temperature. Based on their response to change in temperature, these polymers are categorized in two classes; first, polymers that become insoluble above a critical temperature called the lower critical solution temperature (LCST), and second, polymers that precipitate and undergo phase change below a critical temperature called as the upper critical solution temperature (UCST) (Figure 1.1). When polymers exhibiting LCST are dissolved in an aqueous system, they are completely miscible at normal temperature, but their solubility decreases with increase in temperature and above a critical value, i.e., LCST, they show phase separation (Boutros, Chats, & Kiparissides, 1997; Yan, Zhu, & Kenkare, 2000). These types of materials are also called "negative temperature–sensitive polymers," that is, poly(*N*-isopropyl acrylamide) (PNIPAAm). The second class of polymers, which show UCST, are also referred to as "positive temperature–sensitive polymers"; that is, the temperature above which these polymers remain miscible in solution and as temperature of the solution falls below critical value, phase separation occurs, for example, poly(acrylic acid) (PAA), polyacrylamide (PAAm), and poly(acrylamide-*co*-butyl methacrylate).

4. Smart Inorganic Polymers (SIPs): They are hybrid or fully inorganic polymers with tunable (smart) properties such as stimuli responsive physical properties (shape, conductivity, rheology, bioactivity, self-repair, sensing etc.). The backbones of SIPs are made

from elements other than carbon which can lessen the burden on scarce non-renewable resources and provide more sustainable alternatives. Common backbones utilized in SIPs include polysiloxanes, polyphosphates, and polyphosphazenes, to name a few.

SIPs have the potential for broad applicability in diverse fields spanning from drug delivery and tissue regeneration to coatings and electronics. As compared to organic polymers, inorganic polymers in general possess improved performance and environmental compatibility (no need for plasticizers, intrinsically flame-retardant properties). The unique properties of different SIPs can additionally make them useful in a diverse range of technologically novel applications, such as solid polymer electrolytes for consumer electronics, molecular electronics with non-metal elements to replace metal-based conductors, electro chromic materials, self-healing coatings, biosensors, and self-assembling materials.

- **Smart polysiloxanes**



Polysiloxane, commonly known as silicone, is the most commonly commercially available inorganic polymer. The applications of smart polysiloxanes vary greatly, ranging from drug delivery, to smart coatings, to electrochromics.

- **Drug delivery**

Synthesis of smart stimuli responsive polysiloxanes through the addition of a polysiloxane amine to an α,β-unsaturated carbonyl via aza-Michael addition to create a polysiloxane with N-isopropyl amide side-chains has been reported. This polysiloxane was shown to be able to load ibuprofen (a hydrophobic NSAID) and then release it in response to changes in temperature, showing it to be a promising candidate for smart drug delivery of hydrophobic drugs.

- **Coatings**

Smart properties have also been reported for polysiloxane coatings without metal oxides, namely, a polysiloxane/polyethylenimine coating designed to protect magnesium from corrosion that was found to be capable of self-healing small scratches.

- **Poly-(ε-caprolactone)/siloxane**

Poly-(ε-caprolactone)/siloxane is an inorganic-organic hybrid material which, when used as a solid electrolyte matrix with a lithium perchlorate electrolyte, paired to a W2O3 film, responds to a change in electrical potential by changing transparency. This makes it a potentially useful electro chromic smart glass.

- **Smart phosphorus polymers**

There exist a sizable number of phosphorus polymers with backbones ranging from primarily phosphorus to primarily organic with phosphorus subunits. Some of these have been shown to possess smart properties, and are largely of-interest due to the biocompatibility of phosphorus for biological applications like drug delivery, tissue engineering, and tissue repair.

5. Electro active Polymers: Electro active polymers are an increasingly important class of smart materials that can undergo structural deformations, such as swelling, shrinkage, and bending, in response to an electrical field. Electro responsive polymers can be categorized into two main groups based on their primary activation mechanisms, namely electronic electro active polymers—EEAPs and ionic electro active polymers—IEAPs. EEAPs are driven by external electric fields and by Coulomb forces and include materials such as piezoelectric polymers, electrostrictive polymers, and dielectric elastomers (Martins et al., 2014; Cardoso et al., 2011). Although these polymers require typically high electrical field strengths in the order of 10–100 V μm− 1 for electrostrictive polymers and dielectric elastomers, efforts to reduce driven electric fields are being carried out (Meng and Hu, 2010). Nevertheless, EEAPs feature attractive actuating performance due to their high efficiency, short response time, high durability, stability, and reliability. In turn, IEAPs are driven by the movement of ions or molecules and comprise polyelectrolyte gels, ionic polymer–metal composites, conducting polymers, and carbon nanotubes (although not polymeric). Such materials show the advantages of typically being activated by very low voltage of about 1–5 V. However, they can only typically be operated within a surrounding electrolyte medium (Meng and Hu, 2010; Verbrugghe et al., 2015).

Among the most investigated electro responsive polymers for biomedical applications are polyelectrolyte hydrogels based on both natural and synthetic polymers, with the ability to deform under an electric field due to anisotropic swelling or DE swelling, as charged ions are directed towards the anode and cathode side of the gel. These water-swollen macromolecules feature many advantages. First of all, they present the unique ability to resemble natural

biological tissues because of their hydrophilic nature, soft consistency, and three-dimensional (3D) polymeric network that allow large amounts of water. Moreover, they are stable in aqueous and biological fluids at physiological temperature, pH, and ionic strength, and many of them are biocompatible (Verbrugghe et al., 2015).

Furthermore, they cause minimal mechanical irritation to the surrounding tissue and reduced protein adsorption and cell adhesion are possible due to the rubbery nature of hydrogels and to the low interfacial tension between the gel surface and the aqueous surrounding fluids, respectively. Physically, they have the unique ability to absorb water, which allows them to swell/Deswell to several thousand times their original volume, which in turn makes them extremely interesting for drug-delivery systems because of their ability to release specific volumes of drugs. Finally, depending on the applications and sites of administration, hydrogels can acquire various shapes like rods, disks, films, and micro particles and their physical and chemical properties can vary with composition). Typical natural polymers used to process electro responsive polymers are chitosan, hyaluronic acid, and alginate, while PAA, poly(meth acrylic acid)—PMAA and polyacrylonitrile have been used as synthetic polymers. Additionally, combinations of natural and synthetic components have been also used.

V. CONCLUSIONS

Smart materials are the next generation of materials that have a potential to impact different fields including science, engineering, medicine, and automotive industry. They will have significant impact on civilization. The technology of smart materials is an interdisciplinary, emerging field. A number of technical, peer-reviewed journals are dedicated to publishing information on smart materials. Three of such are Smart Materials and Structures, Smart Material Research, and Journal of Intelligent Material Systems and Structures.

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