Chapter 1

Smart Coatings

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Materials that are capable of adapting their properties dynamically to an external stimulus are called responsive, or smart. The term "smart coating" refers to the concept of coatings being able to sense their environment and make an appropriate response to that stimulus. The standard thinking regarding coatings has been as a passive layer unresponsive to the environment. The current trend in coatings technology is to control the coating composition on a molecular level and the morphology at the nanometer scale. The idea of controlling the assembly of sequential macromolecular layers and the development that materials can form defined structures with unique properties is being explored for both pure scientific research and industrial applications. Several smart coating systems have been developed, examined, and are currently under investigation by numerous laboratories and industries throughout the world. Examples of smart coatings include stimuli responsive, antimicrobial, antifouling, conductive, self-healing, and super hydrophobic systems.

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Introduction

Over the past 25 years, coatings technologies have been influenced by the need to lower Volatile Organic Contents (VOC) as well as to reduce the use of costly petroleum based solvents. Waterborne, powder, UV-curable and high solids coatings have had significant growth. Traditionally, these coatings had the primary functions of protecting and decorating substrates.

In addition to VOC reduction, major efforts have been directed to understanding the basic scientific principles that control coating formulation, property enhancement, and its longevity and durability. Among recent performance related studies, investigation of improving acid etch, corrosion, and scratch resistance are noteworthy. Other research and development contributions have been in raw material design, including polymers made through Atom Transfer Radical Polymerization (ATRP) and novel polymer bound additives. Such developments have enabled formulators to design coatings for specific end-uses and well-defined performance requirements.

In the past few years, coatings research has taken a new turn. Nanotechnology is, of course, still the major technology driver in this area. Such influence is mainly due to the development and availability of innovative particle systems, polyelectrolytes, liquid crystals, conductive polymers, as well as nano-structured sol-gel systems. These innovations are enabling the design of novel coatings with exceptional properties and at the same time, allowing the control of the design of the coating more precisely and on a molecular scale.

More recently, there has been growth in research and development and the commercial product generation of coatings which have novel functions. These products sense and interact with their environment in addition to having the traditional protection and decorative functions. These coatings are often referred to as *smart coatings*. More specifically, a smart coating is one which detects changes in its environment, interacts and responds to changes while maintaining compositional integrity. The changes it may respond to include light, pH, biological factors, pressure, temperature, polarity, etc. Hence, a smart coating is tailored in such a way that one or more of the above listed functions can be "switched on" or "switched off" depending on the type and strength of an external signal. Because of such novel switchable functions, these types of coatings generally offer significant added value.

The two potential driving forces for such developments are the need for microelectronic device miniaturization, and multi-functionality as a surface coating. The driving force of nano-revolution is a continuous progress in microelectronics toward increasing the integration level of integrated circuits (IC) and thus the reduction in size of active elements of IC's. In the last decade the size of active elements (e.g., transistors) have been reduced by a factor of two every 18 months (1). Smart coatings are contributing to such developments and can replace mechanical sensors, reduce the number of moving parts, as well as weight and size reduction.

Science and Technology of Smart Coatings

Multifunctional smart coatings have been developed that sense corrosion, pressure, and temperature (2). Additionally, protective and decorative coatings that are self-healing are in commercial use today. Smart coatings are also playing major roles in medical fields by offering permanent antimicrobial and anti-inflammatory medical devices, including implants and release-on-demand medications. Other examples of smart coatings include but are not limited to reversible thermochromic, piezoelectric paint, hydrophilic/hydrophobic switching, self-cleaning, pH responsive, and self-erasing inks.

As mentioned, major efforts have been directed to designing materials that behave predictably and statically. This means that the properties are permanently defined and the behaviors can be reasonably predictable. This, in effect, ensures the longevity of the material during service. Possible changes in the environment of the material during its use are only taking into account (in such a way, that the material disposes of "**reserves**") to withstand the impact of environmental changes in order to maintain the predefined function. But the property profile is fixed. Here, the “reserves” are viewed as structurally sound and durable polymers such as hydrolytically stable high molecular weight acrylic polymers or certain types of enhancing additives such as ultraviolet absorbers that can inhibit free radical attack and polymer degradation.

High performance conventional coatings use well-designed polymers that take into account the service environment and environmental exposure conditions. For example, an exterior automotive coating must be chip, scratch, corrosion and etch resistant. The chip resistance property is achieved by using tough polymers that dissipate external physical forces and recover quickly upon impact. However, repeated exposure to stone impact gradually reduces the elasticity of the polymer. In this instance, under continuous environmental stimuli, the recoverable elongation shifts toward unrecoverable elongation, yielding a ductile polymer, hence the chip resistance is compromised. This is an example where the reserves are depleted to an extent that the integrity of the system is compromised.

In contrast to the above case, the situation is fundamentally different in nature and biology. Since living beings face continuously new situations, the materials they are made of have to cope with the permanent changes encountered in order to guarantee survival.

In biology, the standard property under variable conditions is assured and maintained by permanent reorganization, rebuilding and reshaping. The growth and healing of bones is an example of such behavior. Alternatively, nature has created materials that change their properties dynamically. These materials communicate with environmental factors and respond to changes by altering their properties and functions to meet the given requirements. Cell membranes are a good example of such responsive materials. Materials which are capable of adapting their properties dynamically to an external stimulus, are called stimuli responsive or “smart materials.” Hence, **smart coating is a coating which**

detects and responds dynamically to changes in its environment in a functional and predictable manner. Many so called smart coatings that do not respond to changes in a dynamic and reversible manner may actually be classified as very high performance and novel coatings.

Smart Coatings can be designed and prepared in many ways such as by incorporating stimuli responsive materials such as light, pH, pressure, temperature, etc. sensitive molecules, nano-particles and antimicrobial agents as additives, or by strategically designing polymer structures and coatings that respond to either internal or external stimuli.

In principle, in order to obtain **responsiveness**, two actions must happen concomitantly as well as selectively (3):

- a stimulus must be initiated and the signal be received by the material
- a chemical or physical process is induced by this signal

In order for the response to be predictable and functional, the stimulus must be clear, specific and unambiguous to ensure that the resultant responses do not interfere or cancel each other all together. Those signals that function by triggering responses within the coating itself and with the aim of modifying the bulk properties are called **internal stimuli** such as those in corrosion sensing or self-healing coatings. Responses that alter the surface characteristics relative to the environment such as in self-cleaning coatings are **external stimuli**.

Signals can either be **momentary** or **continuous**. In the case of a momentary signal, a burst of stimulus just long and strong enough is needed to switch the properties of the material from one state to another. Hence, the material will remain in an altered state until an opposing signal reverts the properties back to the original state. For example, materials that respond to pH changes will require (higher or lower pH) to return to the original state. Smart coatings responding to such stimuli are more challenging to create because the state with modified properties must be fairly stable. In the case of continuous stimuli, the modified properties remain unchanged as long as the signal persists (e.g., pressure or temperature change).

Signal(s) acting on the system may produce a smart and unique behavior which may remain permanently fixed, thus not allowing it to return to the original state under any circumstances. Two clear examples of such unidirectional systems include, self-healing and antimicrobial coatings. Due to availability of monitoring tools, measurement and the convenience of fabrication of unidirectional systems, more of these have been carried out and many more are underway. On the other hand, true two-directional system must be able to switch repeatedly from one state to another and perhaps thousands of times during its service life. Examples of such materials, although rare, are thermochromic and pressure sensing coatings.

Since the signal must work on some organic or inorganic chemical entity (polymer, pigment, additive, etc.,) the stimulus can either be physical or chemical in nature. The physical stimuli can include, light, temperature, electrical field, solubility, acoustic and electromagnetic waves, pH, ionic strength, pressure, electrical and surface tension gradients. The physical signals are abundant, more tunable and perhaps less complicated than the chemical counterparts. The chemical stimuli include acid-base, photochemical, electrochemical, redox, and biochemical reactions as well as chemical bond formation and breakings. While there are multiple chemical reactions that can be used as stimuli, monitoring the extent of reactions, their levels and limits are far more difficult and complex.

Structural or property changes are the ultimate result of stimuli responsive materials or smart coatings. For example, structural or configurational change responsible or color change of a reversible simple system containing diazobenzene is limited to *cis-trans* conformation, while minimal structural change is observed in a silver containing antimicrobial coating.

Examples of smart coatings

Modification of surfaces by chemical and physical means to regulate adhesion, adsorption, wettability, etc., is a well-known and widely used approach (4). The ability to reversibly switch the properties of a solid surface from a strongly hydrophobic to a strongly hydrophilic has been demonstrated by grafting various polymers onto polymeric and non-polymeric solid materials (5). Schematic of surface modification and its response to solvent initiated morphology is shown in Figure 1.

In similar investigations brush-like structures containing polystyrene and poly (2-vinylpyridine), P2VP, were exposed to various agents (stimuli) and the response in wetting properties were measured. For example, after exposure to toluene the surface became hydrophobic and the outer top surface contained polystyrene brushes while after exposure to hydrochloric acid produced a hydrophilic surface containing predominantly polyvinyl pyridine (6).

The well-known pH indicator phenolphthalein changes from colorless to red as the pH rises. This phenomenon has been applied to detect the corrosion of aluminum (7). While reversible systems based on pH –responsive acid-base reactions are more abundant and quite easily accessible, in practice their utility is hampered by their lack of repeatability for more than a few times as salts accumulate over time. In addition, such reactions are sensitive to counter ions found in most coating formulations (8). Examples of acid and base functional polymers are shown in Figure 2.

Acid-based reactions that respond to pH variations have also been used to demonstrate switching behavior of brush-like polymers. To demonstrate such responsiveness, polyacrylic acid (PAA) and poly(2vinylpyridine) polyelectrolyte brushes were grafted to a silicone wafer (9). It was demonstrated that at high and low pH values, Figure 3, the top of the sample is occupied by hydrophilic protonated P2VP and dissociated PAA respectively, therefore, the brush remains hydrophilic in the entire range of pH, except in the neutral region, where a compensation of the charges takes place. In pH 2, PAA brush is hydrophobic

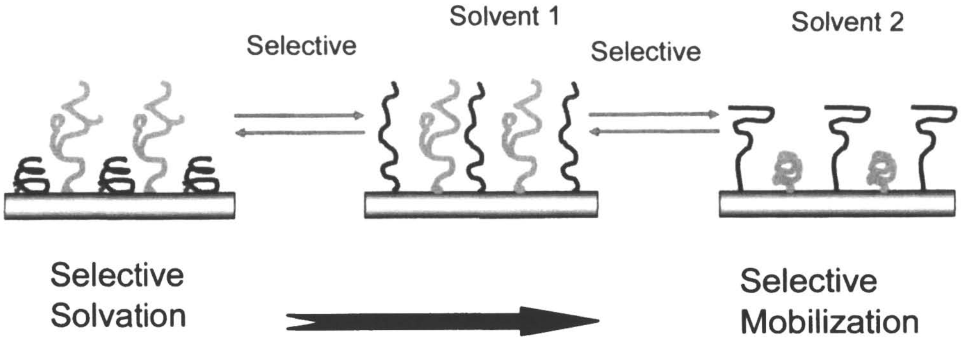

Figure 1. Schematic representation of a solvent initiated morphology change.

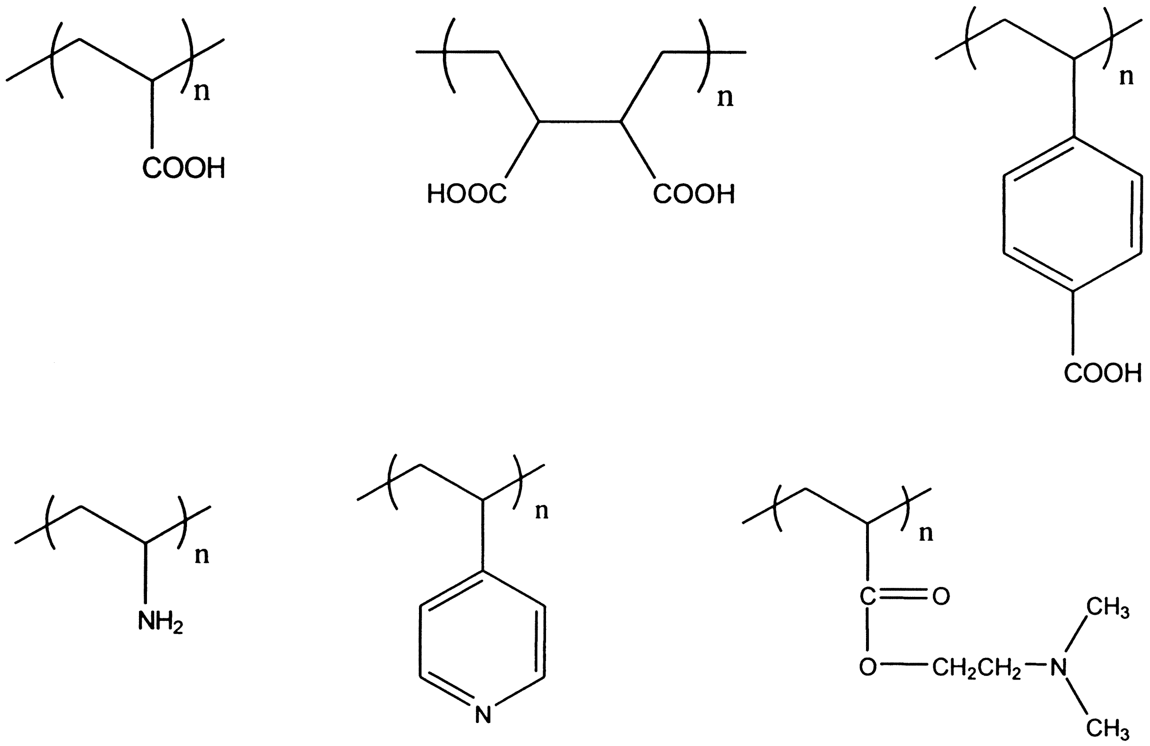

Figure 2. Representative chemical structures of acid and base functional polymers.

with a contact angle of 70°, where at pH 10, it behaves hydrophilic with a contact angle of about 20°, while a P2VP brush demonstrates an inverse behavior. Responsive behaviors of such systems are of potential interest for drug delivery systems and smart nano-devices.

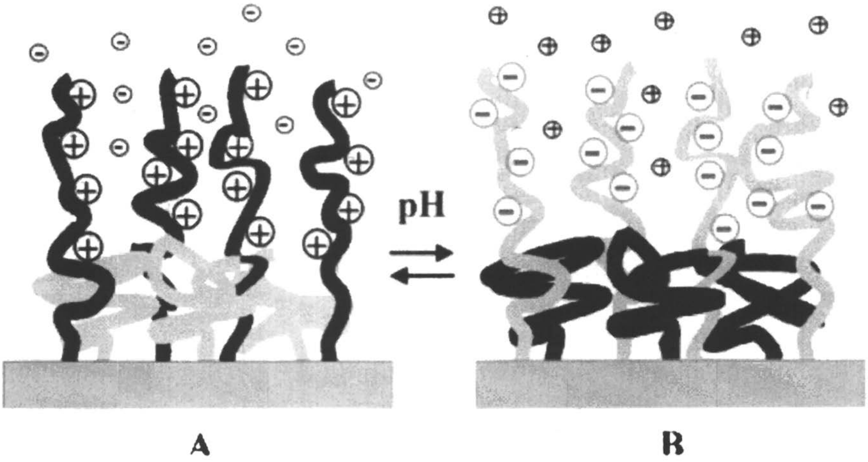

Figure 3. Schematic representation of switching behavior of mixed PE brush upon change of pH: below isoelectric point (A) and above the isoelectric point(B).

Among systems responding to redox reactions, two examples of polyaniline and polythiophene are noteworthy (10). One major advantage of these systems is that the redox reactions produce colored substances.

Photochemical reactions offer a practical approach to reversible systems. As mentioned above, a more stable *trans*-isomer of azobenzene containing coatings (11-12) upon irradiation converts to a *cis*-isomer which can be reverted to the original state by the application of heat and light. Two other systems that are capable of producing photochemical reversible systems are shown in Figure 4.

Organic and inorganic thermochromic pigments and polymers offer a convenient way for designing smart coatings. Certain conjugated polymers and cholesteric liquid crystalline polymers are well-established classes of single component polymers that exhibit thermochromic properties. In some liquid crystalline polymers, under special circumstances, the annealing of the photo-oriented films above the glass transition temperature within the mesophase results in a strong amplification of the optical anisotropy.

Organic dyes can also be incorporated into polymeric systems that switches color as a function of temperature stimuli. For example, a three component

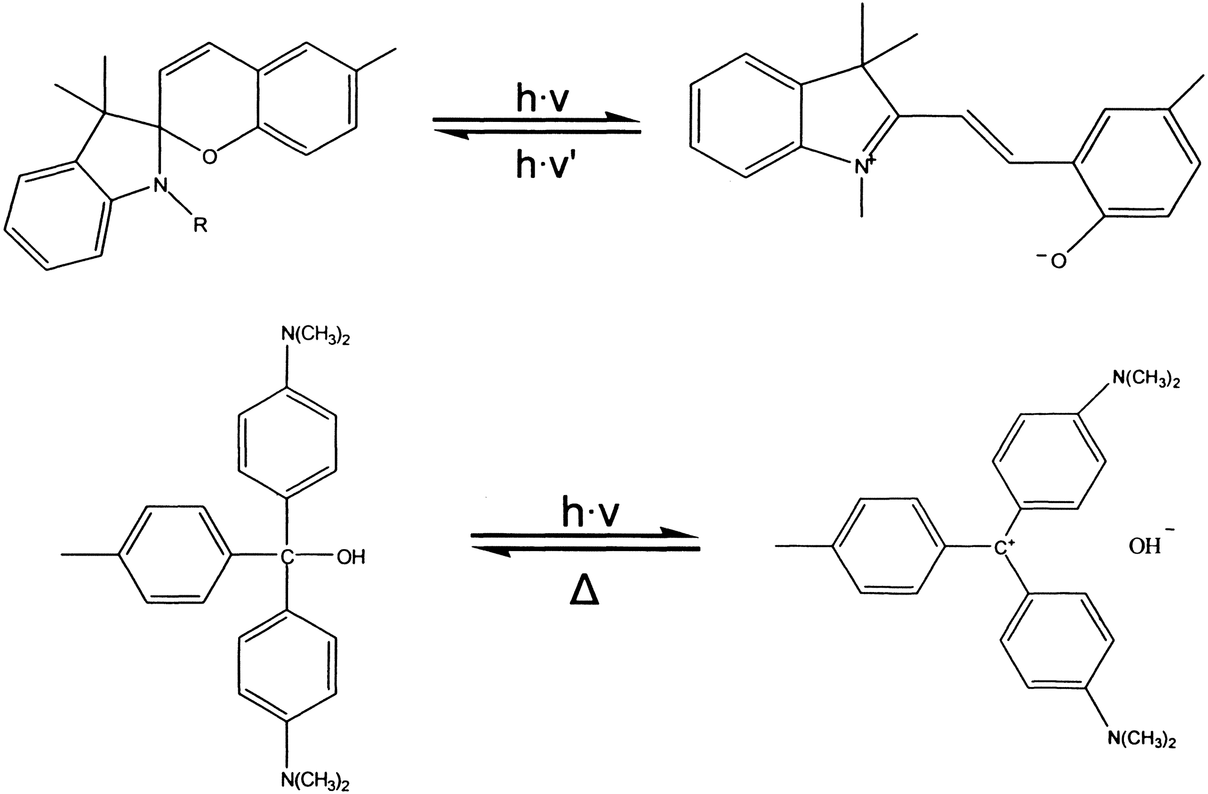

Figure 4. Example of suitable redox switches

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system made of a leuco dye, Figure 5, a developer and a sensitizer shows reversible thermochromism in which the colorless dye is transformed to a colored form by heating in a reversible manner.

As shown in Figure 6 (a), the absorption spectra of such a thermochromic system with polyethylene film exhibits an absorption band in the visible range at about 617 nm at 25 °C that disappears when the sample is heated to 80 °C. The thermochromic behavior is illustrated in Fig 6 (b) in which the blue film at ambient temperature switches to colorless upon dipping in hot water (13).

Reversible thermochromic materials are widely used as safety devices. High temperature, reversible indicators give visible indication that a surface is hot. They are used on radiator caps in automobiles and fire-resistant doors to prevent burns. In addition to industrial applications, the technology has been applied to kitchenware in the form of saucepan handles which change to a red color when they reach about 45 °C.

Photochromic coatings which darken reversibly on exposure to light have already found commercial applications. Most photochromic coating materials are based on organic photochromic materials such as spirooxazine, and pyrans, incorporated into organic polymeric or inorganic composites by a sol-gel process. These coatings with response times of about seconds are applied onto transparent substrates (glass, polymers) or on non-transparent substrates (ceramics, polymers, paper) with dry film thicknesses in the range of 5-50 μm.

Smart window coating materials are characterized by their ability to adjust to light transmission upon application of an electrical potential. Materials used in smart window devices include suspended particles, liquid crystals and electrochromics (14).

Electrochromic materials can change their color when a potential is applied due to electrochemical oxidation and reduction. Both inorganic transition metal oxides such as WO_3 and organic polymers such as [3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine which requires indium tin oxide and vanadium oxide counter layers are employed (15, 16).

Pressure sensing paints (PSP) are comprised of a luminescent dyes and metal complexes such as divalent osmium complexes (17). Ruthenium (18-20).Iridium (21-24), as well as platinum (25-30) as the luminophore. The phosphorescent dyes are usually dissolved into, or are part of a polymer matrix. The sensing functions by oxygen quenching of the excited state; hence, emission intensity varies with changes in oxygen concentration or pressure. When molecules of the above agents absorb quanta of energy they are promoted into an excited state. From this excited state, there are a number of pathways for the molecule to return to the ground state. All of the pathways have consequences as to how the PSP performs. The processes of luminescence and the bimolecular quenching are pathways that allow a PSP to function.

Research and development in unidirectional stimuli responsive coatings have also produced commercially available coatings. Antimicrobial and anti-inflammatory coatings are being used on medical devices (drug eluting), military clothing and on appliances and hospital equipment. Self-healing

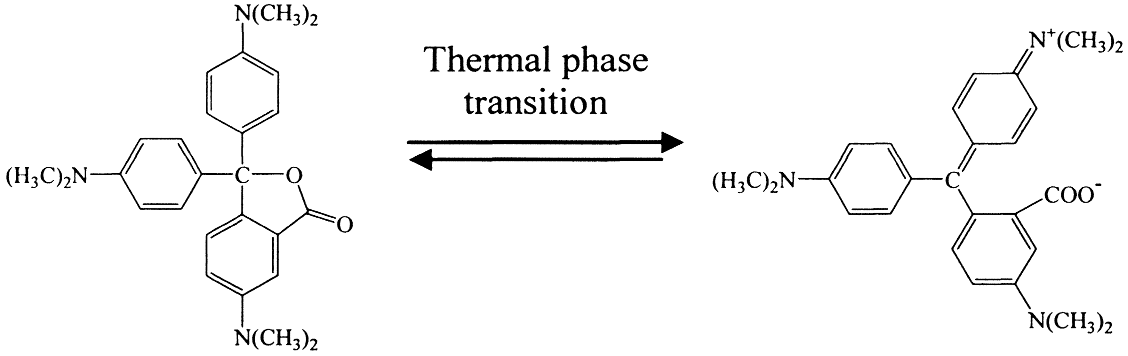
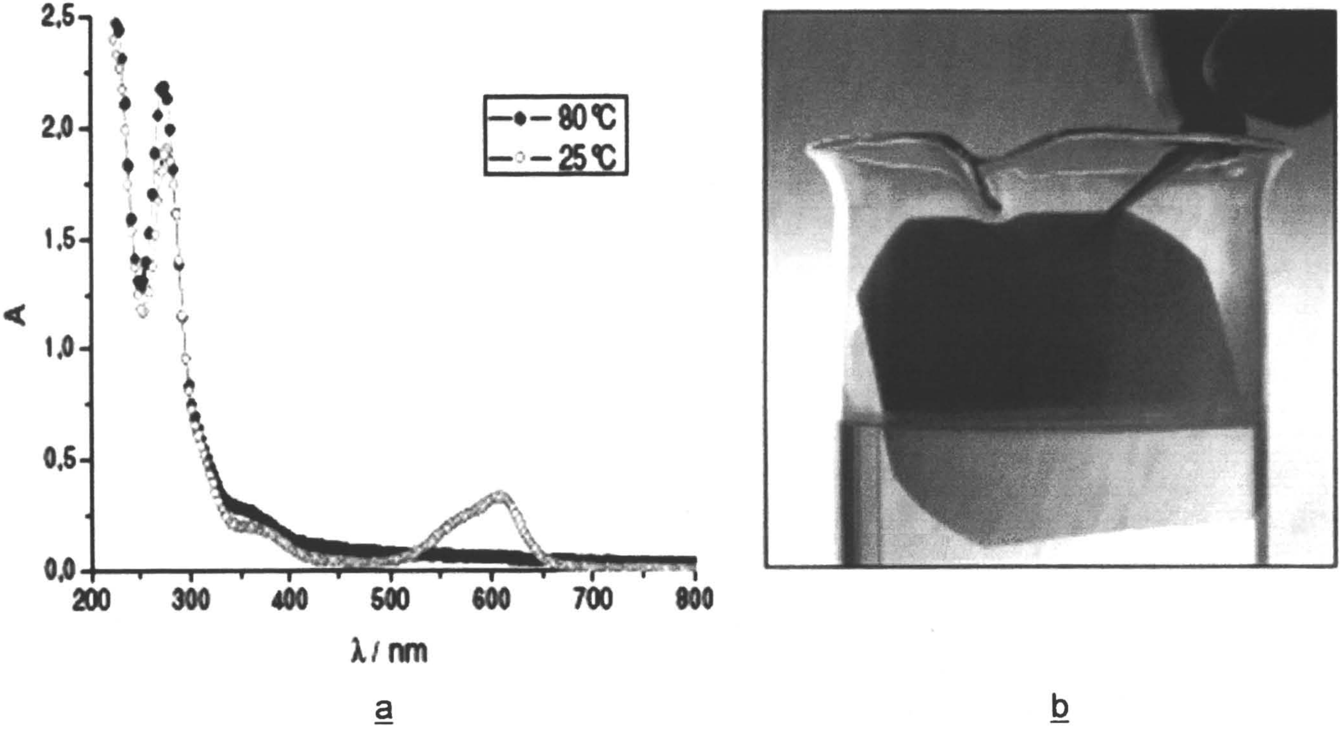


Figure 5. Thermal transition of a colorless leuco dye via ring opening reaction.



a

b

Figure 6. Example of thermochromic thermoplastic film.

coatings, corrosion sensing coatings, radio frequency identification coatings, intumescent coatings, as well as self-erasing inks are examples other unidirectional responsive coatings.

In general, antimicrobial coatings are made either by incorporating biocidal agents into formulation, or polymer structures (31, 32). All of the four classes disrupt the microorganisms' usual activity thereby, rendering it inactive (33). Silver and its various derivatives have been used extensively. (34-42).

Silver containing antimicrobial coatings are made by dispersing a few percent of silver particles either in free form as nano-particles or encapsulated with various porous materials in the polymeric matrix. The antimicrobial activity in these systems arise from the ion exchange, i.e., exchanging ions necessary to cell metabolism with unnecessary silver ion, resulting in disruptions and gradual death (43).

A fair amount of research work and testing along with application has been done with quaternary amine salts. Quaternary ammonium compounds (QAC's) are some of the most commonly used antimicrobials. Common characteristics among QAC's are that they possess both a positive charge and a hydrophobic segment (44-51).

Classification and biological activity of QAC's depend upon the nature of the organic groups attached to nitrogen, the number of nitrogen atoms present, and the counterion (50).

Halamine has been used to coat and produce inherently antimicrobial fibers and surfaces. Halamine must be activated by the addition of chlorine atoms, such as simple household bleach (*52).* A schematic structure of a recent polymeric system containing halamine is shown in figure 7.

Titanium dioxide (TiO_2), is present in three crystalline polymorphs: rutile, anatase and brookite. Anatase crystal is the most photoactive. Cancer cells have been demonstrated to be susceptible to the chemistry of photocatalysis (53). There have been a plethora of studies published on the use of titanium dioxide as a photocatalyst for the decomposition of organic compounds (53-57). Typically the anatase form is utilized in this application, as it is the most photoreactive.

When the TiO_2 photocatalyst is exposed to light in the presence of water vapor, hydroxyl radicals and superoxide anions are formed. Titanium dioxide coatings containing pigment grade or nano-sized particles, therefore, have been used as antimicrobial coatings.

Concern with any additive approach is the loss of active ingredients due to leaching out and migration. To remedy this, various polymeric systems (Figure 8) containing tethered quat amines have been used.

Smart antimicrobial coatings may also be used to coat medical implants that are suspected to cause infection, tissue destruction, premature device failure or the spread of infection to other areas (58-61).

Coatings that can release antibiotics on demand are quite interesting. Many antibiotic-treated medical devices release antimicrobials continuously at high

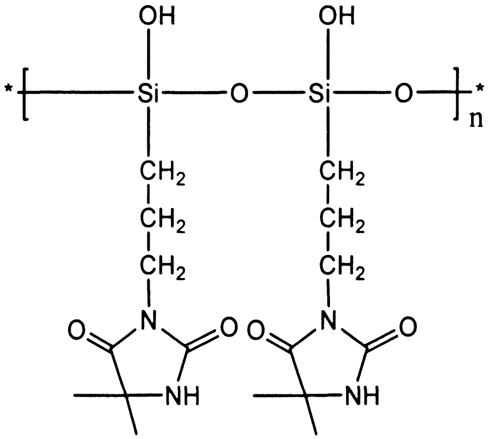
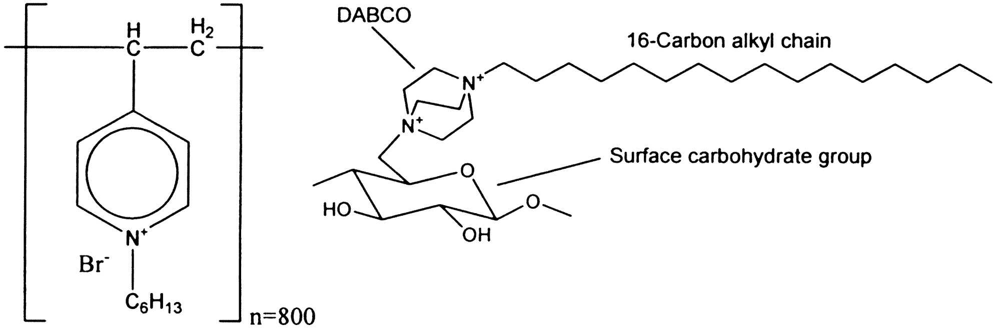


Figure 7. Antimicrobial agent based on halamine derivatives (52).

dose levels, irrespective of whether infection is present or not. An ideal drug delivery system releases a drug at specific locations and at the required time.

Investigations are underway to design a new antibiotic delivery system which could accelerate the delivery of drug containing products under conditions present during an infection. The implantation of a synthetic biomaterial elicits a number of biological responses, one of which is inflammation (62). The polymeric drug delivery system being investigated takes advantage of the enzymes released during the inflammatory process in order to trigger the degradation of the polymer. Subsequently, antibiotic drugs are released which were originally used as actual monomers in the synthesis of the polymer itself. Since the inflammatory response is activated in the presence of bacteria or injury, which may predispose a patient to infection (58), an antibiotic could be released, proportionate to the magnitude of the response. Since polyester-urethanes have been shown to be susceptible to degradation by inflammatory enzymes (63), a polymer containing similar chemistry is targeted as an initial model for this investigation.

Inspired by biological systems such as cells and bones in which damage triggers restructuring, reshaping, rebuilding and healing, structural polymeric materials have been developed that possess the ability to self-heal. In one approach microencapsulated healing agents and chemical catalysts are dispersed in an epoxy coating layer (64-66). When damage occurs in the polymer, a crack propagates through the matrix rupturing the microcapsules in the crack path. The ruptured microcapsules release the healing agent which is then drawn into the crack through capillary action. Once the healing agent within the crack plane comes into contact with the embedded catalyst, a chemical reaction is triggered and polymerization of the healing agent occurs.



N-hexylpoly(4-vinyl-pyridine) DABCO= 1,4-diazabicyclo [2.2.2] octane

Figure 8. Schematic representation of polymeric quaternary amine antimicrobial agents.

Yet another approach (68), takes advantage of ever existing ordinary stimuli in the environment. Most coatings are exposed to atmospheric elements of water, various electromagnetic radiations and a wide range of temperatures. The natural process of mechanical, hygrothermal fatigue and chemical factors degrade coating matrix and initiate mirocracks within a coating. Propagation of microcracks may result in fracture, loss of barrier properties, delamination and coating failure. Schematic representation of coating degradation upon exposure to atmospheric elements and subsequent self-healing is demonstrated in Figure 9.

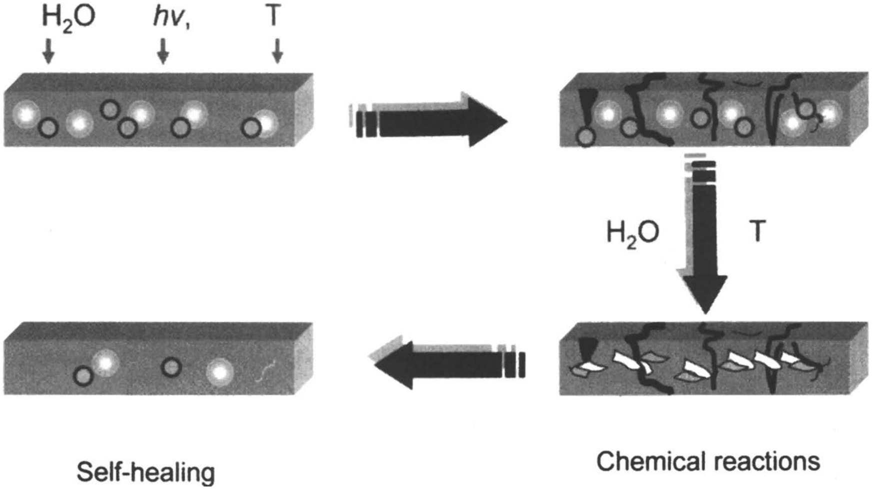


Figure 9. Schematic representation of self-healing sequences in a polymeric coating.

In this approach, microencapsulated healing agents are dispersed in the coating medium. The capsules are designed to rupture and dissolve in water or once exposed to high temperatures. Upon exposure to harsh and abusive conditions such as high temperature and high humidity and mechanical forces, the microcapsules dissolve, melt or rupture and release the healing agents. The reactants are then drawn into the crack through capillary action. Chemical reactions between healing agents take place triggering on-site polymerization and healing of the damaged area. The SEM images of encapsulated healing agents and the cross section of coating containing healing agents are shown in Figure 10.

The healing of the coating is demonstrated by comparing the stress-strain behaviors of exposed and unexposed samples of the coatings. As can be seen from the dynamic mechanical analysis curves in Figure 11, the sample containing self-healing agents responds favorably to exposure conditions by

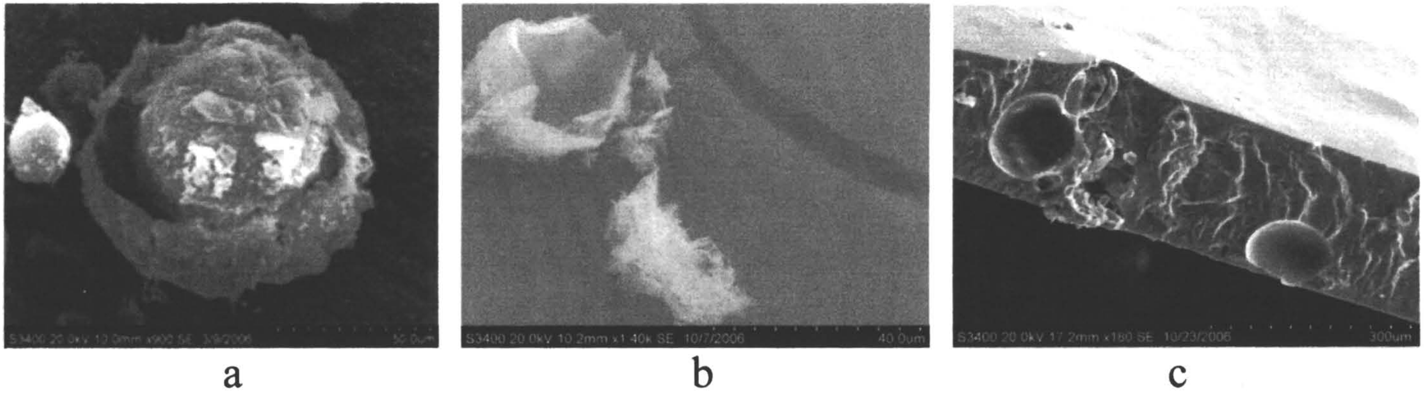
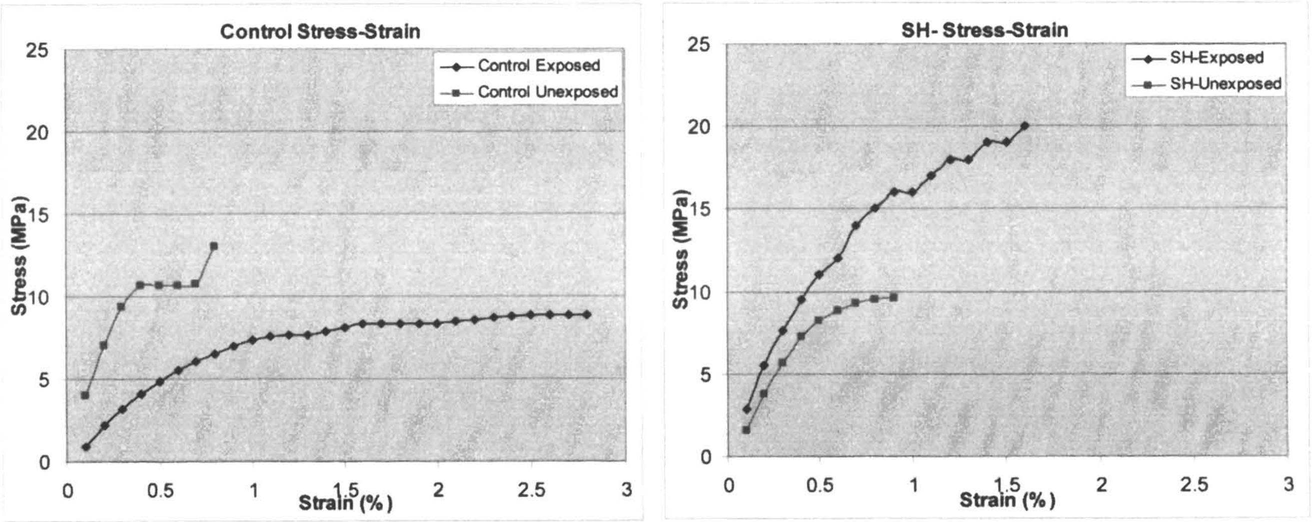


Figure 10. Microcapsule with healing agent (a), release of healing agent on exposure to high humidity and high temperatures (b), embedded microcapsules in coating medium (c)



A

B

Figure 11. Control without healing agent (A), -■- Control unexposed, -◆- Control exposed at 75% RH, 45 °C; sample with healing agent (B), -■- SH-unexposed, -◆- SH-exposed.

increase in modulus, while the control (without healing agent) is apparently plasticized by exposure to water and high temperatures.

A similar trend is also observed when the free-film samples of a control and a self-healing coating are tested according to ASTM D638, tensile properties of plastics and ASTM D1474, indentation hardness test methods. As can be seen from Table I, the average tensile value of the exposed polyurethane coating increases about 5%, presumably due to the reaction of unreacted isocyanate groups accompanied by an expected increase in elongation and reduction in coating hardness due to plasticization by water. On the other hand, exposure of the self-healing coating results in an increase of about 25%, accompanied by negligible increase in elongation and the fair amount of increase in surface hardness.

Table I. Tensile, elongation and surface harness comparison of control and self-sealing coating.

Sample	Tensile (Psi)	Strain %	KHN, Hardness
Control. Unexposed	31.29	14.75	3.38
Control. Exposed*	33.05	16.91	3.32
SH55 Unexposed	32.12	13.77	3.56
SH55 Exposed	40.34	15.13	4.98

* 24 hours at 42 °C, 75% RH

Based on the above preliminary results, it seems obvious that the self-healing property can restore the integrity of a coating which has developed a minor crack as a result of simulated environmental aging.

Conclusion

Smart coatings have been around for much longer than the term itself. These novel coatings offer technological capabilities which conventional coatings cannot. It seems clear from this review that many of the approaches which are now simply interesting research projects will find their way into mainstream coatings applications in the near future.

References

1. Nabok, A. *Organic and inorganic Nanostructures* **2005**, Artech House, MA, USA.
2. Shen, Y.; et al, *Polymer Preprints* **2002**, *43*(1) 69-70.
3. Laschewsky, A.; Lotsch, D.; Seeboth, A.; Storsberg, J.; Stumpe, J. *Smart Coatings III* **2004** European Coatings, Vincentz.
4. Minko, S.; Motornov, M.; Eichhorn, K.; Nitschke, M.; Simon, F.; Stamm, M. *Langmuir* **2003**, *19*, 8077-8085.
5. Minko, S.; Müller, M.; Motornov, M.; Nitschke, M.; Grundke, K.; Stamm, M. *J.Am. Chem. Soc*. **2003**, *125*, 3896-3900.
6. *Minko, S.; Motornov, M.; Eichhorn, K.; Nitschke, M.; Simon, M.; Stamm, M. Langmuir*, **2003**, *19*, 8077-8085.
7. *Zhang, J.; G. Fenkel, J. paper presented at the Material research Society meeting, Boston*, **1997.**
8. Laschewsky, A.; Lotsch, D.; Seeboth, A.; Storsberg, J.; Stumpe, J. *Smart Coatings III*, **2004** European Coatings, Vincentz.
9. Minko, S.; Houbenov, N.; Stamm, M. *Macromolecules*, **2003**, *36*, 5897-5901.
10. Anton, P.; Heinze, J.; Laschewski, A. *Langmuir*, **1993**, *9*, 77-85.
11. Anton, P.; Laschewski, A.; Ward, M. *polym. Bull.* **1995**, *34*, 331.
12. Laschewski, A.; Ward, M. *polymer*, **1991**, *32*, 146.
13. Pieroni, O.; Ciardelli, F. *Trends in polym. Sci.*, **1995**, *3*, 282.
14. Laschewsky, A.; Lotsch, D.; Seeboth, A.; Storsberg, J.; Stumpe, J. *Smart Coatings III*, **2004** European Coatings, Vincentz.
15. Xu C.; Liu L.; Legenski S.; Ning D.; Taya M. *J. Mater. Res*., **2004**, *19*(7), 2072.
16. Welsh D. M.; Kumar A.; Meijer E. W.; Reynolds J. R.; *Advanced Materials*, **1999**, *11*(16), 1379.
17. Xu C.; Tamagawa H.; Uchida M.; Taya M.; *Proceeding of SPIE*. **2002**, 4695, 442.
18. Carlson, B.; Phelan, D. *Smart Coatings*, **2005** Proceedings, Coatings Research Institute, Ypsilanti, Michigan, USA.
19. Puklin, E.; Carlson, B.; Gouin, S.; Costin, C.; Green, E.; Ponomarev, S.; Tanji, H.; Gouterman, M., *J. App. Poly. Sci*. **2000**, *77*(13), 2795.
20. Ji, H-F.; Shen, Y.; Hubner, J. P.; Carroll, B. F.; Schmehl, R. H.; Simon, J. A.; Schanze, K. S., *Appl. Spect*. **2000**, *54*(6), 856.
21. Gouin, S.; Gouterman, M., *J. App. Poly. Sci*. **2000**, *77*(13), 2815.
22. Vander Donckt, E.; Camerman, B.; Hendrick, F.; Herne, R.; Vandeloise, R., *Bull. Soc. Chim. Belg*. **1994**, 103, 207.
23. Amao, Y.; Ishikawa, Y.; Okura, I., *Anal. Chim. Acta*, **2001**, *445*, 177.
24. Gao, R.; Ho, D. G.; Hernandez, B.; Selke, M.; Murphy, D.; Djurovich, P. I.; Thompson, M. E., *J. Am. Chem. Soc*. **2002**, *124*, 14828.

25. DeRosa, Maria C.; Hodgson, Derek J.; Enright, Gary D.; Dawson, Brian; Evans, Christopher E. B.; Crutchley, Robert J., *J. Amer. Chem. Soc.* **2004**, *126*(24), 7619.
26. Jiang, F.; Xu, R.; Wang, D.; Dong, X.; Li, G., *Gongneng Cailiao* **2000**, *31*(1), 72.
27. Schanze, K. S.; Carroll, B. F.; Korotkevitch, S., Morris, M., *AIAA J.* **1997**, *35*(2), 306.
28. Jiang, F-Z.; Xu, R.; Wang, D-Y.; Dong, X-D.; Li, G-C.; Zhu, D-B., Jiang, L., *J. Mat. Res.* **2002**, *17*(6), 1312.
29. Sakaue, H.; Gregory, J. W., Sullivian, J. P., *AIAA J.* **2002**, *40*(6), 1094.
30. Bowman, R. D.; Kneas, K. A.; Demas, J. N.; Periasamy, A., *J. of Microscopy*, **2003**, *211*(2), 112.
31. Schanze K. S.; Carroll B. F.; Korotkevitch S.; Morris M., *AIAA J.* 1997, 35(2), 306.
32. Tiller, J. C.; Lee, S. B.; Lewis, K.; Klibonov, A. M. *Biotechnol Bioeng* **2002**, *79*, 465-471.
33. Lin, J.; Tiller, J. C.; Lee, S. B.; Lewis, K.; Klibanov, A. M. *Biotechnol Lett.* **2002**, *24*, 801-805.
34. Donelli G.; Francolini, I; *J. Chemotherapy,* **2001**, *3*(6): 595-606.
35. Klasen, H..J., *Burns*, **2000**, *26*, 131-138.
36. Bromberg, L.E., V.M. Braman, D.M. Rothstein, P. Spacciapoli, S.M. O'Connor, E.J. Nelson, D.K. Buxton, M.S. Tonetti, and P.M. Friden. *J. Controlled Rel.* 2000, 68, 63-72.
37. Quintavalla, S., and L. Vicini, *Meat Science* **2002**, 62:373-380.
38. Wright, J.B., K. Lam, D. Hansen, and R.E. Burrell. *Am. J. Infect. Control* **1990**, *27*:344-350.
39. Clement, J.L. and P.S. Jarrett. *Metal-Based Drugs* **1994**, *1*, 467-482.
40. Thurman, R.B. and C.P. Gerba. *CRC Critical Reviews in Environmental Control* **1989**, 8, 295-315.
41. Yahya, M.T., L.K. Landeen, M.C. Messina, S.M. Kute, R. Schulz, and C.P. Gerba. *Can. J. Microbiol.* **1990**, *36*, 109-116.
42. Becker, R.O. *Metal-Based Drugs* **1999**, *6*, 311-314.
43. Maki, D.G., and P.A. Tambyah, Emerg. *Infect. Dis.*, **2001**, *7*:1-6.
44. Feng, Q. L., Wu, J., Chen, G.Q., Cui, F.Z., Kim, T. N., Kim, J.O, *J. Biomed Mater Res*, **2000**, *52*, 662-668.
45. Tiller, J.; Lee, S.; Lewis, K; Kilbanov, A., *Biotechnology and Bioengineering* **2002**, *79*, (4) 465-471.
46. Li, G. J.; Shen, J. R.; Zhu, Y. L. *J Appl Polym Sci.* **2000**, *78*, 668.
47. Gabrielska, J.; Sarapuk, J.; Przestalski, S.; Wroclaw, P. Tenside, *Surfactants, Detergents*, **1994**, *31* (5), 296.
48. Robertson, J. R. Eur. Pat. 0,611,782, A1, **1994**.
49. Talaro, K.; Talaro, A., *Foundations in Microbiology*; WCB Publishers: Dubuque, IA, 1993; pp. 286.

50. Tiller, J. C.; Liao, C. J.; Lewis, K.; Klibanov, A. M. *Proc Natl Acad Sci*. **2001**, *98* (11), 5981.
51. Li, G. J.; Shen, J. R.; Zhu, Y. L. *J Appl Polym Sci*. **2000**, *78*, 668.
52. Cohen, J. I.; Abel, T.; Filshtinskaya, M.; Melkonian, K.; Melkonian, A.; Burkett, D.; Engel, R. Abstracts of Papers, 223rd ACS. National Meeting; Orlando, FL, 2002; CARB-059.
53. Lin, J.; Winkelmann, C.; Worley, D.; et al., *J. Appl. Polym. Sci*. **2002**, *85*, 177-182.
54. Sunada K., Watanabe T., and Hashimoto K., *Environ. Sci. Technol.* **2003**, *37*, 4785-4789.
55. Blake, D.M., P. Maness, Z. Huang, E.J. Wolfrum, and J. Huang. *Bull. Environ. Contam. Toxico*. **1999**.
56. Matthews, R. W., *J. Chem. Soc. Faraday Trans.* I. **1989**, *85*:1291.
57. Carey, J. H., J. Lawrence, and H. M. Tosine. *Bull. Environ. Contam. Toxicol*. **1976**, *16*:697.
58. Turchi, C. S., and D. F. Ollis. J. Catal. **1989**, *119*, 483.
59. Gristina AG. *Science*, **1987**, *237*, 1588.
60. Dankert J, Hogt A.H, Feijen J., Biomedical polymers, CRC Crit Rev Biocomp, **1986**, *2*, 219-301.
61. Buret A, Ward KH, Olson ME, Costerton JW., *J. Biomed Mater Res* **1991**, *25*, 865-874.
62. Dickinson GM, Bisno A.L., *Antimicrob. Agents Chemother.* **1989**, *33*:597.
63. Anderson J.M., *Cardiovasc. Pathol.,* **1993**, *2*, 334.
64. Santerre JP, Labow RS, Duguay DG, Erfle D, Adams GA. *J. Biomed. Mater Res* **1994**, 28, 1187-1199.
65. White, S.R., Sottos, N.R., Geubelle, P.H., Moore, J.S., Kessler, M.R., Sriram, S.R., Brown, E.N., and Viswanathan, S., *Nature*. **2001**, *409*, 794.
66. Brown, E.N., Sottos, N.R., White, S.R. *Experimental Mechanics* , **2002**, *42*, 372.
67. Kessler, M.R., Sottos, N.R., White, S.R. *Composites Part A*., **2003**, *34*, 743.
68. Unpublished report.