Advancing Controlled Release Packaging through Smart Blending

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Researchers from Rutgers University and Clemson University have collaborated to develop a concept of using smart blending to generate functional packaging films for the controlled release of active compounds such as antimicrobials, antioxidants and flavour compounds to extend the shelf-life of food. In this paper, literature results are reviewed to justify the significance of controlled release packaging (CRP) and the research gaps for further development are identified. A major research gap is the lack of packaging materials that can provide the release of active compounds at rates suitable for a wide range of food packaging applications. Smart blending is a promising technology for bridging this research gap. To fully realize the potentials of smart blending, a systematic approach for developing CRP using smart blending is also presented. Copyright © 2005 John Wiley & Sons, Ltd.

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INTRODUCTION

Controlled release packaging (CRP) is a new generation of packaging materials that can release active compounds at different controlled rates suitable for enhancing the quality and safety of a wide range of foods during extended storage. The basic concept is to use the package as a delivery system for active compounds, such as antimicrobials, antioxidants, enzymes, flavours and nutraceuticals. The term CRP refers broadly here to the packaging materials and to the technology or applications associated with them. Two important examples of CRP, antimicrobial packaging and antioxidant packaging, will be focused upon in this paper.

CRP belongs to a group of food packaging technologies known as active packaging.¹⁻⁷ Traditional packaging serves, for example, as a gas barrier, providing passive protection against the transmission of oxygen and water vapour. Active packaging provides additional functions that in some way enable the package to interact with the food to improve food quality, safety and convenience. CRP is an active packaging technology because it provides the additional function of controlled release of active compounds. Other active packaging technologies include oxygen scavengers,⁸⁻¹⁰ carbon dioxide scavengers,¹¹,¹² polymer films with selective gas permeabilities,¹³ and microwave susceptors.⁶ Active packaging is now recognized as a useful tool for food quality and safety enhancement.

Among the active packaging technologies, CRP is one of the most innovative and challenging. Controlled release of drug delivery has been used for some time,¹⁴⁻¹⁷ and procedures for achieving release under various conditions are well-
established. Studies have been reported on modelling drug delivery devices for pharmaceutical applications. However, significant research on testing the concept of controlled release of active compounds from food packaging did not appear until the last decade. CRP is particularly attractive for controlling food degradation reactions that are continuous and increase exponentially, such as microbial growth and lipid oxidation, because constant replenishment of inhibitory compounds prevents runaway deterioration of safety and quality. There is a variety of active compounds that can potentially be used for CRP, e.g. nisin, tocopherols, potassium sorbate, sodium benzoate and others. Research and development of CRP is anticipated to grow rapidly with the advent of new polymer materials and antimicrobials.

The purpose of this paper is to review the evidence that justifies the development of CRP, identify some of the major research gaps, and present a possible new approach to bridge the research gaps. Although this paper refers frequently to antimicrobial packaging and antioxidant packaging (two of the largest applications of active packaging), the same basic principles and discussions are also applicable to packaging containing other active compounds.

**JUSTIFICATION FOR CRP RESEARCH**

The motivation for developing CRP is to prolong stable shelf-life without adding excess additives to foods. Traditionally, active compounds such as antimicrobials, antioxidants and anti-browning agents are incorporated into initial food formulations. A limitation of this traditional method is that once the active compounds are consumed in reaction, protection ceases and the quality of food degrades at an increased rate. Another limitation is its inability to selectively target the food surface where most spoilage reactions occur; as a result, an extra amount of active compound is also unnecessarily added inside the food product. CRP can overcome these two limitations by continuously replenishing active compounds to the food surface, compensating for the consumption or degradation of active compounds, so that a pre-determined concentration of active compound is maintained in the food to achieve a desired shelf-life. Since the release of active compounds is directed toward the food surface, smaller amounts of active compounds are needed. Reducing the amount of active compound in the food may also provide improved quality of the flavour, since many additives give a burning and/or off-flavour.

**Antimicrobial packaging and evidence for effectiveness**

Antimicrobial packaging is a promising and rapidly emerging technology in which antimicrobial agents are incorporated into or coated onto food packaging materials to prolong the shelf-life of the packed food, usually by extending the lag phase and reducing the growth rate of microorganisms. Several categories of antimicrobials have been tested for antimicrobial packaging applications: organic acids, fungicides, bacteriocins, proteins, enzymes, inorganic gases, species, silver substitute zeolite, and others. Our research group has also studied the antimicrobial activities and release kinetics of packaging materials containing paraben, triclosan and nisin. In general, the studies reported in the literature confirm that antimicrobial packaging is effective in inhibiting microbial growth and extending the shelf-life of food.

To justify the further development of antimicrobial packaging, the behaviour of hazardous food-borne microorganisms in the presence of antimicrobial packaging must be understood. As alluded to earlier, antimicrobial packaging is essentially a system that enables ‘slow addition’ of antimicrobials to the food, as opposed to ‘instant addition’ when the antimicrobials are added directly to the food formulation. The question is how microorganisms respond to these two different delivery modes. Is it better to add the antimicrobial into the film or directly in the food?

Recently, we have studied the sensitivity of *Listeria monocytogenes* under three delivery modes of nisin (Figure 1): (a) instant addition of nisin (200IU/ml) into broth medium to simulate the situation when nisin is added to the food formulation; (b) slow addition of nisin into broth medium using a pump to simulate the situation when nisin is released slowly from the package; and (c) a combination of the above two deliv-
ery modes (▼). The control (●) is cultured in the absence of nisin. The instant addition causes almost immediate kill (5 log) followed by outgrowth of the survivals, mostly mutants and adapted cells.35 Slow addition of the same amount of nisin over 100 h does not cause any dramatic reduction in viable cell count; however, survivals are not nisin-resistant mutants but the cells that are temporarily adapted to the presence of nisin in the environment.35 Combined delivery mode provides the most effective microbial inhibition over time, indicating that slow addition can work synergistically with instant addition. These results also imply that CRP can be an effective means to enhance food quality and safety.

**Antioxidant packaging and evidence for effectiveness**

Antioxidant packaging is another major type of CRP, in which antioxidants are incorporated into or coated onto food materials to reduce oxidation in the packed food. Antioxidants impregnated within plastic films have been shown to increase the storage stability of oatmeal cereal42 and vegetable oils.43 Currently, manufacturers add the antioxidant BHT, so that slow release of BHT from the package will help extend the shelf-life of the food product. The use of antioxidant packaging has also been proposed to reduce lipid oxidation in milk.44 While milk contains low concentrations of natural antioxidants, such as α-tocopherol (13–30 μg/g milk fat) and ascorbic acid (<20 ppm), processing and storage deplete these natural antioxidants, necessitating the addition of exogenous antioxidants for retarding the onset of lipid oxidation.45,46 Although the antioxidants may be added directly to milk in one large dose, a drawback of this approach is the rapid depletion of the antioxidants.47,48 Controlled release could help to delay the depletion of the antioxidants.

In recent years, there has been a growing interest in the use of natural antioxidants in food packaging applications, especially tocopherols. Tocopherols, commonly known as vitamin E, are non-toxic compounds with a positive public perception, broad regulatory approvals, and environmentally friendly appeal to the consumer. Tocopherols are effective antioxidants for food products, including pork patties,49 ground beef,50 peanut oil51 and many others. The incorporation of high levels of α-tocopherol into LDPE film has shown to inhibit oxidation of a linoleic acid emulsion stored in contact with the film.52–54 The retention of α-tocopherol in LDPE and PP depends on the type of polymer as well as the fat, alcohol and organic acid contents of the food product.55 Besides being an effective antioxidant for reducing oxidation in foods, tocopherols are also excellent stabilizers for polymer processing.56–59 During the manufacturing of plastic bottles or films, the shear and heat input necessary to melt the polymer often causes bond-breakages of the polymer molecules, leading to undesirable reactions.60 The free radicals generated from the bond-breakages can attack other polymer molecules, or react with oxygen in air to form oxygen-containing low molecular weight compounds, such as aldehydes and ketones. These compounds, which are entrapped in the polymer matrix, can evaporate in air as off-odour volatiles or migrate to food as off-flavour compounds. It has also been shown that α-tocopherol can act as a highly effective antioxidant to minimize the formation of these off-flavour compounds.60–62 Therefore, tocopherols can serve dual functions when added to packaging: as a stabilizer for polymer processing and as an antioxidant in CRP to reduce oxidation.
RESEARCH GAPS

Although the evidence from the above sections suggest that CPR is a promising technology, its potential cannot be fully realized unless all major technical problems are overcome. It is commonly acknowledged by researchers in this field that a major hurdle is the inability to deliberately control the release of active compounds at rates suitable for different food systems and degradation reactions. There are the following two major research gaps leading to this situation:

- **Lack of suitable packaging materials.** Traditional packaging materials are primarily developed for strength and afford little to provide the function of controlled release. Most existing packaging materials consist of single polymers that have inherently limited ranges of properties compared to those of polymer blends. Existing technologies of polymer coating, film casting and lamination are found to produce CRP materials with limited ranges of release rates, i.e. the release rates of active compounds are either too slow or too fast. The release rate is slow when migration is governed by diffusion in the polymer matrix, and it is fast when governed by swelling or dissolution.\(^3^3,3^4\) It is not uncommon that a large portion of the active compound incorporated in these materials will never be released, because of the closely packed structures of polymer matrices and/or strong affinity between active compound and polymer. A new approach is needed to overcome the limitations of existing materials and film technologies.

- **Lack of a systematic research approach.** While the effectiveness of CPR has been demonstrated, the research studies so far are mostly empirical in nature. A logical next step is to more systematically examine the major factors governing the controlled release of active compounds. These major factors include the composition of the film and active compounds, the effects of processing conditions, the microstructure of film, and the control release and other properties of the film. A better understanding of these factors will greatly facilitate the design of CRP systems.

Presented in the next section is a new approach consists of using polymer blends to overcome the limitations of single polymers and using smart blending to generate novel packaging materials suitable for CRP. A systematic research approach is also outlined (see Figure 4) to illustrate how novel CRP may be developed using smart blending.

A NEW APPROACH: SMART BLENDING

Before introducing the concept of smart blending, it is helpful to mention that the microstructure or morphology of a polymer film can greatly influence the mobility of active compound in the film. This is particularly true for a polymer blend film consisting of two or more immiscible phases, where a new approach is needed to alter the blend morphology in order to provide controlled release of active compound for a wide range of food applications, such as short-term or intermediate-term inhibition of microorganisms in fresh foods and long-term reduction of lipid oxidation in processed foods.

**Smart blending** is a new technology developed at Clemson University for developing films with numerous morphologies from polymer blends. The smart blending system (Figure 2) consists of two extruders and a *smart blender* that is composed of a barrel and internal motor-operated stir rods (Figure 3A). Two separate polymer melt flows from the extruders are combined at the smart blender. Various morphologies can be developed progressively by rotating each rod alternately and periodically.\(^6^3\) This is a structuring process, not a mixing process. The blending of two or more polymers provides a wide range of film properties. What makes the system ‘smart’ is that the structuring is not random – the same morphology is always produced under a given set of conditions (through computer control) – which allows the development of a predictable set of relationships. A single smart blending device can produce a large variety of structures in plastics that are often unattainable with conventional compounding equipment, post-processing operations or time-consuming iteration.

The operation of the smart blender is based on the principle of chaotic advection, a relatively new field of fluid mechanics introduced about 20 years ago,\(^6^4,6^5\) in which two confocal elliptical cylinders
rotate to set up a flow pattern characterized by repetitive stretching and folding of polymer melts, so that intricate patterns emerge (Figure 3). The blend morphology development can be controlled via specification of stir rod motions relative to the melt residence time in the smart blender. Figure 3A also illustrates the progressive development of morphologies: thick layers are stretched and folded to form multilayer morphology. More interestingly, other useful and novel derivative blend morphologies can also be obtained from the breakup of the multilayer (see Table 1). Chaotic advection is now established as a subtopic of fluid mechanics, with wide ramifications and promises in material processing and other applications. Recently, it has drawn interest as a prospective technology for the manufacture of nano-scale materials.

Table 1 shows some examples of film morphologies recently developed by Zumbrunnen et al. using smart blending. It is important to note that a variety of blend morphologies are producible at single compositions with smart blending. This differs starkly from conventional compounding equipment, where morphology and composition are strongly coupled. For example, at low (e.g. 20% by volume) compositions, the minor polymer component is formed into droplets in twin screw extruders; however, with a smart blender, multilayer, interconnected layer, platelet, fibre and droplet morphologies are all producible. The influence of composition on properties can thereby be deter-
Table 1. Film morphologies developed using smart blending

Multilayer morphology
Melt-processable polymer components can be arranged into numerous layers of desired thickness and number. Highly layered films with very thin internal layers, as shown, can have low permeation properties due to enhanced crystallinity resulting from crystalline morphology changes.68,70

Selective permeable morphology
Multilayer films such as the one shown can be produced where layers of one polymer component contain small holes to allow selective permeation. The average sizes of holes are adjustable via process control. The holes also mechanically connect adjacent layers to prevent layer delamination.68

Interpenetrating (sponge) morphology
Tough films can be produced by creating morphologies having dual phase continuity. Because such films are formed by new means, compositional restrictions imposed by conventional processes are greatly reduced. Such novel morphologies can also have selective permeability.63,66

Fibrous morphologies
The highly layered morphologies can be converted in the smart blender to fibrous morphologies. The number and aspect ratio of fibers are large. Such fibres can serve as internal reinforcements or electrical conductors when formed from an electrically conducting plastic.63,72

Conducting networks
Electrically conducting networks among conducting particles such as carbon black are assembled in situ to render extruded films conducting at low additive concentrations.73,74 Food packaging additives and inert fillers may also be added to create networks useful for CRP.
mined independently of structure by producing films having the same morphology and different amounts of the minor polymer component. Unlike conventional compounding equipment, dual phase continuous (i.e. interpenetrating\textsuperscript{63,66}) blends are producible with less restriction on composition. Opportunities also exist to develop films with selective gas permeabilities by controlling the composition and development of the interpenetrating structure.

**SYSTEMATIC RESEARCH APPROACH**

Figure 4 outlines a systematic approach for using smart blending to develop CRP. There are four important components: the compositions of active compounds and polymers, processing conditions, microstructure of films, and properties of films. A better understanding of the relationships between these components will greatly facilitate the successful developing of CRP.

- **Composition.** This refers to the selection of the active compound and the polymer blend. The stability of the active compound is an important consideration, since smart blending involves the high shear/thermal extrusion process. A way to minimize degradation is to add the active compound through the smart blender instead of through the extruders. The use of polymer blends offers many possibilities. Two or more different polymers and sometimes fillers may be used. The concentrations of the major and minor polymers may be varied. Immiscible polymers are often selected for generating a wide range of morphologies.

- **Processing.** Recent advances in smart blending technology have enabled precise control of the smart blender to achieve a variety of blend morphologies. The viscosity ratio and interfacial tension of the polymer components are useful parameters in determining the initial processing conditions, and the influence of these two parameters on structure development are known from computational models.\textsuperscript{75} Viscosity ratio is typically defined as the ratio of minor component viscosity to major component viscosity. A ratio between 1 and 15 is desirable to form blend morphologies with sub-micron features and a variety of different types (e.g., multilayer, interconnected network, dual phase continuous, platelet, fibrous, and droplet). Interfacial tension acts to resist deformations imposed by the smart blender but is also responsible in part...
for driving morphology transitions that make possible the production of the numerous morphology types.

- **Structure.** This refers to the microstructure (or morphology) and crystallinity of the polymer film, as well as the dispersion of active compound in the polymer film. The microstructure of the film may be characterized by scanning electronic microscopy (SEM). Since the CRP film developed using smart blending consists of immiscible phases, it is important to determine the dispersion of active compound in these phases. However, techniques for characterizing the dispersion of active compound in polymer films are not available. It may be possible to develop techniques to determine the localization of active compounds by fluorescence emission in confocal microscopy or by infrared mapping.

- **Properties.** The most important property of CRP is the release kinetics. The release of active compound from a CRP film involves three steps: molecular diffusion within the film toward to the film/food interface, mass transfer across the interface, and dispersion into the bulk food. In most cases, diffusion is the slowest or rate controlling step. Diffusion of small molecules (such as O₂ and H₂O) in a polymer film is known to depend on the size and shape of the diffusing molecule and properties of the polymer such as density, crystallinity, tortuosity, degree of crosslinking and branching, and glass transition temperature. Diffusion of larger molecules such as tocopherols and nisin is more complicated, especially for polymer blend films consisting of two or more immiscible phases. The release kinetics may be measured for various food simulants (e.g. water, ethanol, and oil emulsions) and different temperatures, and the data may be used to estimate diffusion coefficients and partition coefficients. It is also important to determine the efficacy of the active compound and formation of any degradation, compounds after the film making process. Physical properties such as seal strength and tensile strength are also important.

The major purpose of this approach is to establish the quantitative relationships between composition, processing, structure and properties. These relationships will help to develop CRP with a wide range of release rates. The application of CRP to a particular food system requires knowledge of the required release rate, which is defined as the rate of release of active compound from the package to the food necessary to achieve a desired product shelf life under certain storage conditions. The design objective is to closely match the release kinetics of a CRP material to the required release rate of a food system.

**CONCLUSIONS**

Smart blending presents a new paradigm for developing novel packaging materials for the controlled release of active compounds. As mentioned earlier, existing packaging materials used for CRP research have been limited mostly by the use of single polymers. Smart blending offers many more possibilities by using two or more polymers and sometimes fillers. It also offers the ability to deliberately manipulate the film morphologies to provide a wide range of properties. A better understanding of the relationships between composition, processing, structure and properties will significantly benefit the development of CRP. The new understanding may also benefit other research areas where polymer blends maybe used, such as high barrier films for protecting foods from the deteriorative effects of oxygen and water vapour, packaging films with selective permeabilities to oxygen and carbon dioxide for accommodating the respiration and transpiration of fresh produce in modified atmosphere packaging, transdermal patches and selective permeable film for membrane separation. Results in this exciting research will be published by our collaborative team from Rutgers University and Clemson University.

**REFERENCES**


