Role of plastics additives for food packaging

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Abstract
Purpose – The purpose of this paper is to review the new trends in plastic additives, with special focus on developments in food packaging materials.
Design/methodology/approach – Phenomenological research has brought awareness and increased insight into the role of various plastic additives on the packaging of foods. The approach is based on the current trends and the industrial protocols for the additives used in plastic polymer processing for the development of food packaging materials.
Findings – Packaging of foodstuffs is a dynamic process which continually responds to the changes in supply and demand which are the result of adaptations to the varying demands of the consumer, changes in retail practices, technological innovations, new materials and developments in legislation, especially, with respect to environmental concerns. A wide range of additives is available for enhancing the performance and appearance of food packaging, as well as improving the processing of the compound. Polymer additives are important areas of innovation for packaging materials.
Originality/value – The paper reviews and summarizes the recent developments in the functionality of different additives, along with their advantages and disadvantages, currently being used to enhance the properties of food packaging materials that can positively influence the environment within the packaging for the increased demand for raw or processed foods.

Keywords Packaging materials, Additives, Plasticizers, Antimicrobials, Antioxidants, Antifogs

Paper type General review

Introduction
In modern times, packaging has been identified as an integral part of processing in the food industry. Food package is the physical entity that functions as the barrier between the contents and the exterior atmosphere (Smith et al., 1990). Packaging has three tasks:
1 protection (active packaging);
2 information (intelligent packaging); and
3 transport.

Several packaging materials are currently being used for food products, but plastics are the best choice for food processors due to several reasons. Plastics, synthetic, polymeric products of the petrochemical, coal or gas industry; can be moulded into any shape, are aesthetically pleasing and have low density and friction co-efficient (Soroka, 2002). Apart from synthetic polymers, biopolymers such as starch, proteins, cellulose, chitosan, etc. are also available which are intended to be more sustainable, eco-friendly and biodegradable. However, so far these biomaterials have not been able to replace plastics due to a number of technical and economic advantages being offered by them to the manufacturers. Plastics are made from polymers; chemical compounds composed of long molecules made up of chains of small repeat units (monomers). Along with copolymers and physical blends of various plastics, additives are enjoying a key position in determining the quality of packaging materials. Polymers are rarely used alone and hence additives are incorporated to enhance the appearance, to improve the strength and thereby change the characteristics of different plastics in accordance with end use. Additives are the growing sector of the speciality chemical industry. Desirable improvements in polymer performance have opened the door for new and innovative ways of production processes. Several additives provide improved processing and manufacturing performances while others allow polymeric materials to have an assortment of enhanced properties (Murphy, 2001).

The permeability of the packaging material is one of the most critical features of the package for affecting the quality of the food product. Materials can be selected to provide an extended shelf life at an affordable price with excellent barrier properties. Therefore, knowing the important factors for material selection, based on permeability, is an essential part of the package design process. The traditional passive packaging is not effective in protecting food products because of the approach towards food distribution and storage. Furthermore, the extended shelf life of processed foods, stringent food additive regulations and the consumers demand for minimal addition of preservatives to food products have led to the innovation of active packaging. Major active packaging technologies that exist and widely established are based on the use of: oxygen scavengers, moisture regulators, ethylene absorbers, ethanol and carbon dioxide emitters as well as antimicrobial systems (Vermeiren et al., 1990).

Migration of compounds from the packaging into the product, causing off-odours, off-flavours, or other compounds, may pose a risk if migration occurs under conditions that can cause regulatory concerns. Another interaction that could affect the quality and/or safety of the products is sorption of product components into the packaging. Some of these interactions can eventually affect the overall integrity of the package and hence the product. Additives have a significant role in moulding the functionality and barrier properties of plastic packaging materials used in food industry. Moreover, the use of additives has increased tenfold due to growing demand of tailor made plastic packaging for product specific properties.
Additives in packaging materials

The polymer industry has experienced a number of changes throughout the years, starting with the discovery of natural polymers and evolving into the specialised industry that is seen today. Organic polymers such as natural rubber, beeswax and bitumen have been used for centuries, but the materials were unable to be used for general applications because of either being too brittle or soft and therefore unsuitable for use in packaging materials in native form (Williamson, 1994). This led to focus on modification of polymer properties so that these materials would have improved characteristics, allowing their wider use as packaging materials. For example, celluloid was considered to be the first semi-synthetic polymer and in order to make its commercial use, its brittleness was improved with camphor (Williamson, 1994). Today, both natural and synthetic polymers rely on additives to create the new blends of particular characteristic and are mixed with polymer resins to produce high quality packaging materials (Ram, 1997).

Additives are rapidly becoming the miracle workers for the plastics industry, whether they are traditionally used as plasticisers, impact modifiers and antioxidants or in new technologies such as nanocomposites and antimicrobials; their importance is increasing but at the same time a lot of safety concerns have been raised with regard to food applications. Additives are basically categorized by the functions that they perform rather than their chemistry (Table I). The processing of thermoplastics and/or their end-use performance can be greatly enhanced through the use of various additives. Some additives are already present in commercial resins, yet significant benefits can be derived from further modification of those compounds (Foldes and Szigeti-Erdéi, 1997). In addition, the use of the additives affords the processor an opportunity to tailor the material for a specific application. Processing aid type additives improve productivity of the machinery through reduction of internal friction (lubricants), change in the polymer morphology (nucleating agents), foams formation (blowing agents), or suppression in thermal decomposition during processing (antioxidants). Other type of additives are used to enhance aesthetics (blowing agents, optical brighteners), or performance properties of the final parts (flame retardants, antistatic agents, ultra-violet light stabilisers). Lubricants, plasticisers, scavengers are the major additives (depending on their use) while antistats, antioxidants, heat stabilisers, processing aids are minor additives. Modification of the properties of the polymers through the addition of various additives is economically preferable for the introduction of new plastics (Murphy, 2001).

Oxygen scavengers

For several food and beverage products, oxygen is detrimental to product colour, taste and nutrients, besides allowing growth of moulds and bacteria (Singh et al., 2011a). O2 scavengers are being used to protect foods from oxidation of sensitive components like fatty acids, carotenoids, meat pigments and vitamins. O2 scavengers are widely used as sachets inside the package but can be directly integrated into the walls of packaging materials. Passive O2 barriers can slow the ingress of oxygen, but active O2 scavengers absorb oxygen that is in the package closure or walls. Oxygen scavenger technologies are optimised for one or the other task: barrier (active barrier) or headspace oxygen absorption but often both properties are desired for most of the applications (Rooney, 1981). The use of O2 absorbers is a relatively new trend in additives technology for food packaging (Abe, 1994). Elemental iron powder is currently being used as commercial O2 scavenger and is available in several forms such as powders enclosed in sachets, incorporated into the packaging polymer or a polymer layer extruded as part of the package; to maintain freshness by absorbing headspace O2 or oxygen that enters the package (Goldhan, 2006). Ciba® Shelfplus™ O2 oxygen scavenger (now owned by Albis Plastics) is a polymer-based additive that can be incorporated directly into a separate non-food contact layer of the walls of the package (Ciba Archives, 2009). It can be incorporated either into an existing layer within the package or as a distinct scavenging layer. One of the benefits of this technology is that the active O2 scavenging is automatically triggered when it comes into contact with moisture present in the package either from filling.
or retort processing. As it gets activated through moisture, it is
found to be quite effective for high moisture foods (HMF) and
beverages. The system contains iron and salt, both being critical
for inhibition of migration of components to food (Morvillier,
2006). This technology may be implemented with little or no
modification to existing packaging lines but it may not be
suitable for direct food contact (Broydy, 2004). Cryovac® OS is
an oxygen scavenging technology that incorporates the
polymer-based O₂ scavenger OSP™ from Chevron Phillips
into packaging films. It consists of an oxidisable resin, ethylene
methyl acrylate cyclohexene methyl acrylate (EMCM) and a
masterbatch containing a photoinitiator and a cobalt salt
catalyst (Ching et al., 2000). Because it is moisture activated, it
is quite effective and does not degrade into compounds that
cause off-taste or odour and the photo initiator allows the
inactive polymer to be stored and then activated by UV light
during the package filling process. Cryovac® OS Films are being
used commercially in a variety of applications in North
America. In baked goods and fresh pasta, OS Films extend
product shelf life and prevent mould growth. For food products
having longer shelf life such as snack foods, nuts and dried
meats, OS Films prevent discoloration and flavour changes in
the product. The European market currently tends to require
shorter shelf life than the North American market, because
products tend to be distributed over short distances and sold
more quickly. OS Films offer European consumers several
refrigerated foods with exceptionally high quality fresh food.
For modified atmosphere applications with initial moisture
content of 2 per cent, Cryovac® OS Films can reduce O₂ to less
than 0.1 per cent, typically in three to ten days. Cryovac® is in
the process of obtaining approval for OS Films in Asia, and sees
strong growth opportunities in replacing O₂ scavenging sachets,
which are used heavily in the region. In any geographic region,
incorporating the O₂ scavenger film eliminates the problem of
consumers accidentally eating sachets. Also, unlike iron-
containing sachets, OSP (O₂ scavenging polymer) films
contain no metals that can interfere with metal detection
systems used to prevent metal contamination in foods.

Growing use of O₂ scavengers for compounding into PET
food and beverage packaging has increased the number of
packaging suppliers. Amosorb® (ColorMatrix Europe Ltd)
oxygen scavenging technology is used in both monolayer and
multilayer PET bottles for applications such as juice, hot tea,
beer and food applications (El Amin, 2006). Other commercial
O₂ scavenging technologies for PET include MXD6 aromatic
nylon, which can be used as passive barrier as well as active O₂
scavenger. However, in monolayer PET containers, colorants
and additives may interfere with O₂ scavengers, particularly
metal-assisted active barrier systems.

A drive for growth in food packaging is the shift from local
butchers and produce suppliers towards central packaging.
Centralised packaging is advanced in the USA, but has also
begun to take hold in Europe (Markarian, 2006). Though the
potential for degradation and adulteration of food products
exists, the use of O₂ scavengers minimises these negative effects
thereby resulting in shelf life extension. Many options available
in the O₂ scavenging technology have widened their
application arena depending on the type of food material.
Additionally, more natural options exist as in the case of
enzymatic oxygen scavengers. The potential safety and
financial benefits that O₂ scavengers lend to a product line;
makes them a viable solution for standard packaging
applications. Although it is still considered as an emerging
technology, much remains to be learned about its potential
application in other food industries and systems to further
utilize its advantages. Currently sachets are the main source of
O₂ scavenging technology. However, through emerging
polymer and film technology, films are moving to the
forefront of O₂ scavenging applications.

Antimicrobials
Foods are spoiled by a variety of bacteria and fungi, but only
particular microbial species typically attack each type of food
product and generally on food surfaces (Kim et al., 2008).
Active packaging, where the antibacterial agent is immobilised
tightly, is the answer to consumers demand for food without
preservatives. Packaging equipment and material suppliers are
focusing their efforts on developing packaging systems that
are more aggressive and proactive in protecting food from
microbial contamination (Appendini and Hotchkiss, 2002;
Singh et al., 2011b).

The antimicrobial active packaging technology is based on
antimicrobial agents that are immobilised with the polymeric
structure or incorporated in plastic resins, before film casting.
This technology can be divided into two types: preservatives that
are released slowly from the packaged materials to the food
surface or preservatives that are firmly fixed (with disadvantage
of low effect) and do not migrate into the food products. Both
are assumed to control the growth of undesirable microorganisms.
Among the common microorganisms that contaminate food
and beverage products are E. coli, Staphylococcus aureus,
Campylobacter, Salmonella, Clostridium perfringens and Bacillus
cereus. Development of different kinds of active packaging is
under intensive progress (Vermeiren et al., 2002; Van Beest et al.,
2002). One of the key problems of the active packaging
technologies resides in the controlled release of the antimicrobial
agent from the polymer film (Choi et al., 2001; Joerger, 2007).
Antimicrobial additives used in active packaging systems to
slow microbiological degradation of food products have been
the subject of intense research and publicity, but several
concerns have slowed widespread commercialisation in Europe
and the USA. However, Japan has been historically a leader in
antimicrobial applications. Allylisothiocyanate, a naturally
occurring compound in horseradish and wasabi, is used as an
antimicrobial in commercial packaging in Japan, but its use is
limited outside of Asia because of its strong odour. Chlorine
dioxide is used commercially in sachets whereas compounding
into the product is not commercially established (Day, 1998;
Floros et al., 1997). The use of antimicrobials (or biocides) in
packaging is a growing trend in the global food packaging
industry. In USA, many of the antimicrobials in use protect the
packaging or the packaging raw materials, although recent
interest has been in antimicrobials to protect the packaged food
(Appendini and Hotchkiss, 2002). The FDA under the Federal
Food, Drug and Cosmetic Act (FFDCA) regulates
antimicrobials that are incorporated into food packaging.
Under the FFDCA, the FDA ensures that such antimicrobial
applications are safe with respect to any potential human
dietary intake. Unrelated to federal requirements under the
FFDCA, antimicrobial products used in food packaging that
have no intended antimicrobial effect on the processed food in
the package are subject to EPA registration as pesticides under
the Federal Insecticide, Fungicide and Rodenticide Act
(FIFRA). Antimicrobials added to food or delivered to food
via the packaging are treated as direct additives and are not
subjected to FIFRA.
Nisin is produced commercially under the trade name Nisaplin® by Aplin-Barrett in the UK, and can be compounded into the packaging polymer or applied as a powder or a coating. It is widely used in Europe but not extensively in the USA, although it has FDA approval. Silver compounds are also used in Europe and have FDA approval for some applications. Other research is looking at additives that produce the antimicrobial chlorine dioxide under certain relative humidity or UV light conditions. The advantage of these systems is that the antimicrobial could protect any product within the package, not just what comes in contact with a protective coating (Suppakul et al., 2003). The additives are currently being used in a sachet inside the package, but can be compounded into the packaging polymer (Ellis et al., 2006).

Han (2000) reported silver and zinc zeolites among the most popular compounds as antimicrobial packaging materials. Zeolites are complex chemical structures that trap ions, such as zinc and silver, and slowly release the ions into the surrounding environment. Zinc- and silver-containing zeolites can also be incorporated into the packaging material. These compounds are incorporated into cloth, paper, and laminated pouches. When the packaging film comes into contact with the meat, the zeolites release the zinc and silver ions (nano silver ions are under strong criticism by German Risk Assessment Agency), which disrupt the normal biochemistry of the microbial cells. In addition to the effect of zinc and silver ions on microbial growth, some zeolites convert O2 in the wrapped product into ozone (a reactive form of O3), which further inhibits microbial growth. Several years ago, Japanese food technologists developed a zinc and silver ion zeolite-containing cloth for home use. Consumers used to wrap fresh raw meat or poultry in the cloth to prevent the meat spoilage. Consumers can wash the cloth 2,000 times without losing antimicrobial activity. Another natural compound that is effective against mould and yeast is mustard (a kind of proteins produced by microorganisms that possess antimicrobial activity) as food preservatives (Ming et al., 1997; Kim et al., 2002; Scott and Taylor, 2006).

Combinations of antimicrobials provides better efficacy. The research has to move in the direction of highly active combinations of antimicrobials and their cost effective approach. When antimicrobial films fail to remove high numbers of unwanted microbes, they can act as an additional, post-processing safety measure. Several antimicrobial packaging films should be able to provide antimicrobial activity even during or after such processing steps as heat or pressure treatments, and should exert antimicrobial activity on the surviving microbes. In addition, antimicrobial films could allow processing to be done at lower temperatures or pressures, thus reducing processing costs without compromising food safety. In the end, the acceptance of particular antimicrobial films by the food industry will probably depend on the regulatory climate and the balance between the cost of the antimicrobial film and the benefit of a second antimicrobial hurdle.

**Antioxidants/stabilisers**

Plastics are very different from each other as far as their inherent resistance to oxidation is concerned. Differences in stability against oxidation may arise not only from the broad variety of chemical structures of polymers, but with a given polymer, from differences in the manufacturing process (nature and amount of catalyst residues) and in morphology (crystallinity and orientation). Addition of antioxidants is the most common method of stabilisation. Antioxidants are chemical entities, which react with radicals, stop the chain reactions and thus retard the resulting aging of the polymer (Boersma, 2006). Usually, they are effective at concentrations of a fraction of 1 per cent. It is desirable to add the antioxidants as early as possible in the life cycle of a polymer, e.g. before the drying stage of the polymers.

Antioxidants are used in every kind of plastic, but polyolefins account for about 60 per cent of global demand. In all, antioxidants have a $1.3$ billion market globally, and volumes of about 500 million pounds. Their growth in the market is about 4 per cent, tracking the entire polymers sector. The major types of antioxidants are the primary antioxidants-butylated hydroxytoluenes (BHT) and other hindered phenols and the secondary antioxidants – phosphites and thiostearics. Phosphate-phosphonites are generally regarded as the most effective stabilisers during processing, protecting both the polymer and the primary antioxidant. Hydrolytically stable phosphites are the most frequently-used processing stabiliser in high performance additive systems. Primary and secondary antioxidants are used in combination (Boersma, 2003).

For applications in contact with food, US FDA and German BGA (Bundesgesundheitsamt) regulations recommend liquid antioxidants based on Vitamin E. These have been developed as patented systems and also open up new areas of application, in polyolefins and polyurethane foam systems (Demertzis and Franz, 1998). Development in recent years has centred on technical improvement of the product, and easier handling and dispersion. The main technical objectives have more durable effect at lower dosage levels, with good retention of colour and transparency. Improvement of toxicological properties, for food contact and medical applications, has also been a continuing aim of processors and developers. For improved handling, pelletized and liquid systems have been introduced and there is a general trend towards greater use of masterbatch. The most expensive stabilisers are organotin stabilisers (Zweitel, 1998). Systems with better colour fidelity and handling properties are among recent developments. Typical is Dover's Doverphos HiPure 4 – a high purity tris-nonylphenyl phosphite (TNPP) processing and heat stabiliser, which is claimed to reduce overall costs. With 0.1 per cent residual nonyl phenol,
it is FDA-approved for food contact applications and is also used in medicals, colour-critical polyolefins and styrenic block copolymers. It is also effective in acrylics, elastomers, nylon, polycarbonate, polyurethanes, polystyrene, PVC, and PET. A solid phosphate antioxidant has been developed and introduced by GE Specialty Chemicals in its UltranoX range. Designed to meet the demand for a high activity stabiliser with superior hydrocarbon stability and improved handling characteristics, it is based on butyl ethyl propanediol chemistry, rather than the usual pentaerythritol and is approved by FDA for food contact in certain applications and is expected to find applications in polyolefins, styrenics, PVC, engineering thermoplastics, elastomers and adhesives. Recently, GE Specialty Chemicals introduced two new, high performance antioxidants, which perform well under harsh conditions such as gamma irradiation of food packaging. Some companies are using vitamin E antioxidants for improved organoleptic properties for sensitive applications such as plastic milk and beverage bottles. Butylated hydroxyanisole (BHA) and the related compound butylated hydroxytoluene (BHT) are phenolic compounds that are often added to foods to preserve fats from oxidation. Oxygen reacts preferentially with BHA or BHT rather than oxidising fats or oils, thereby protecting them from spoilage. It is used in packaging materials to preserve food odour, colour, and flavour. The phenolic antioxidants, used for long-term heat stability, are also effective processing stabilisers for polypropylene (PP). In the early days of PP, BHT was used extensively to provide or to improve processing stability. Combinations of BHT and high molecular weight antioxidants are still in practice. However, they are increasingly replaced by combinations of high molecular weight phenolic antioxidants and phosphites-phosphonites (Shlyapnikov and Kiryushkin, 1996).

It is understood that the commercial antioxidants are already in use for a long time and going to retain their dominating market share with common plastics. This can be attributed mainly to an excellent price/performance ratio and generally worldwide regulation for use in plastics with food contact. The supply of additive blends, tailor made for specific applications, is expected to rise further in developing countries. More efforts are required in the development of antioxidant systems that can be used in practice for the stabilisation of engineering plastics.

Colorants
Colorants are an essential component in most forms of packaging, and they are critical to extraction and toxicity (Gächter and Müller, 1993). Fortunately, there are some pigments with satisfactory performance that are accepted for food contact applications. Dyes are transparent and give bright colours in light. Most have relatively poor light-fastness and limited heat stability, but will tend to retain their colour better than pigment systems. This is because, with all colorants, it is the surface layer that is affected by exterior conditions such as light. In parallel, dyes also suffer similar fading on the surface than their transparency gives a real depth of colour unaffected by surface influences (Williamson, 1994). Dyes can also be subject of colour migration, which is the matter of legislation for critical products, such as food contact applications and toys.

Thermochromic and photochromic pigments
Are micro-encapsulated liquid crystal systems, giving precise colour-changes at specific temperatures, or when exposed to light. They are particularly interesting for food/pharmaceutical packaging, giving an indicator of storage. Thermochromic pigments change colour with temperature, and there are compounds and master batches for injection, blow moulding or extrusion. The pigments comply with FDA food contact regulations and can be used for novelty products and products requiring warning indicators, such as baby bottles, thermometers and kettles. Possible colour changes are: green to yellow, magenta to blue and coloured to colourless. Typical ranges include Hanna-Victor’s Chameleon organic pigment concentrate for polyolefins and styrenics, with activated colour changes in 10°C bands, from −25°C to +58°C, and a range from Sibner Hegner, which changes from coloured to colourless at 5-15°C or 65-75°C.

Intelligent heat protection
For food products is offered by a pigment system, which has been developed by Sachtleben Chemie GmbH, Germany. It can be incorporated in the plastic films and food packaging materials, to control the temperature in heat-sensitive products. Visible light is kept away and heat may escape unhampered from the package. The product is said to be of interest for projects sponsored by the World Health Organization, aimed at prolonging the preservation of foodstuffs in developing countries, and for disaster relief operations.

High colour strength
Recent development of pigments with very high colour strength, for use to give opacity in thin wall packaging, have taken place according to the needs of food packaging. For example, BASF’s range of azoic yellows (Paliotol) allows bright tints to be produced, which are resistant to heat and light and suitable for food contact. The classes of Paliotol yellows based on isoindoline, and reds based on perylene can be used in polyolefins and in the more technical plastics. A new mixed-phase rutile yellow pigment (introduced by Bayer: Lightfast Yellow 62R) differs from conventional chrome rutile yellows by higher tinting strength, better hiding power and gloss promotion, suitable for lightfast, water-stable and heat-stable pigmentation of plastics and coatings and satisfying purity requirements for food contact applications. A novel blue-shade red azo pigment, Engel tone 1115 (Engelhard) is an alternative to high performance organics, complying with FDA limits for food contact and comparable in heat stability with many high performance bright reds, such as DPPs (up to 300°C in ABS) – which could replace up to 50 per cent savings (Murphy, 1996).

Plastics have completely discarded the stigma of being regarded as “substitute materials”. In close cooperation with the mechanical engineering industry, plastics manufacturers and processors have developed modern processing technologies that have opened up almost unlimited design opportunities with plastics. Colour can increase the attractiveness of the final packaged product and consumer appeal. In pigment research, the search for new structures and pigment stabilisation is in progress, while the price/performance factor is coming increasingly to the forefront. The market potential for pigment preparation will continue to rise due to their biological nature.

Lubricants
Thermoplastic processing of polymeric materials is carried out at temperatures above their crystalline melting point or, in the case of amorphous polymers, above their glass transition temperatures. The macromolecular structure of these
materials is such that the melts have high viscosity and can therefore only be conveyed and shaped under pressure. The resulting shear leads to dissipation of mechanical energy. At points of high flow resistance, in particular, the heat generated can accelerate degradation reactions or adversely affect the dispersion of multiphase systems. The possibilities for optimising the processing properties of plastics through monomer selection, molecular weight control and macromolecular structure are very limited. The primary considerations in polymer development are the required properties and cost. Solving processing problems entails not only selecting the right combination of machine and mould but also using lubricating additives, lubricants, which influence the melt rheology in the desired way. Lubricants are processing aid additives, which are capable of reducing internal and external friction in the molten polymer. The flow of material become less constricted, and melts fracture less likely. This results in the shear heat reduction, better packing and better quality of the parts (Murphy, 2001). Additionally, lubricants also function as mould release agents, thus allowing for faster cycle times in injection moulding.

In addition, the changeover from glycerol to polyols such as pentaerythritol, whose esters have a higher thermal stability due to their structure, marks the start of progress to provide products for more demanding applications. Unsatisfactory compatibility, particularly in the case of the long chain carboxylic acids that have a highly effective lubricating action, often causes cloudy. It can be improved by forming derivatives with molecular units closely akin to the plastic being modified. Hence, the lubricant manufacturers are coming up with numerous developmental products, e.g. with aromatic esterification components (Connors and Pandit, 1978). Another avenue of development has led to reactive lubricants which are protected against migration, volatilization, etc. by chemical development has led to reactive lubricants which are (Connors and Pandit, 1978). Another avenue of development has led to reactive lubricants which are protected against migration, volatilization, etc. by chemical development has led to reactive lubricants which are 

Pigment & Resin Technology

Role of plastics additives for food packaging

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Slips and antistats

Slip and antistats are key components of most packaging, especially flexible packaging. Antistatic agents are used in plastics in order to prevent a build up of static electric charge on the surface of plastic parts. This charge is normally formed during production and handling of those parts. It will tend to attract dust from the ambient air, thus subtracting from aesthetic value of the part. This problem is especially objectionable in consumer-oriented products such as packaging of plastic bottles. Antistats facilitate dissipation of the static charge thus significantly reducing dust accumulation. The use of antistats gives the processor some additional benefits such as better mould release (Murphy, 1996). Antistats are recommended for use in polyolefines polyamides and other resins. The additives are difficult to predict and control because migration occurs over time and depends on part thickness and polymer crystallinity but Ampacet introduced non-migratory, surface-functional slip and antistat products that fit a need for controllable, predictable performance in premium films. Other advantages of the slip include their use at high temperatures than conventional slips and have no adverse effect on sealing. The non-migratory antistat does not interact with adhesives, high thermal stability and has no effect on sealing or printing. Their antistatic properties last longer than those of conventional migrating antistats and its surface resistivity is similar at 50 and 12 per cent relative humidity. The non-migratory additives are used at much higher levels than traditional additives and are more expensive. They find use in coextruded structures, such as a film that has slip on the inside but not on the outside. One trend for antistatic additives is the use of long chain materials for polymer additives (Gächter and Müller, 1993). Long chain antistats provide high temperature processing stability, which is in increased demand as extruders are pushed at faster rates. Trend for slip additives is to use high purity slips with reduced short chain (four to nine carbon) impurities. These high purity slips have lower organoleptics, or taste and odour components. Croda recently introduced a low organoleptic erucamide slip product called Incroslip® that has advantages for the bottled water and beer industries. Plastic screw-type bottle closures contain high amounts of slip to enable torque release. Irradiation or sterilization of bottles by UV or ozone can degrade the trace amounts of by-products inherent in erucamide and produce off-tastes and odours. Incroslip® has improved stability and is less susceptible to degradation than standard torque-release products.

The antistats global market is about $130 million and £60 million, with growth rate of 4-5 per cent per year. Permanent antistatic agents are growing faster than migratory antistatic agents. Their growth is being driven by strong sales of document-handling office equipment and electronic equipment while other antistatic agents (fatty acid esters) are growing robustly for the plastics industry at 6-7 per cent per year because of their role as processing aids for polypropylene and PVC. If the finished product comes into contact with food material, migration aspects of antistatic agent must be taken into consideration. This has led to intense research on the safety aspects of these compounds and their migration in different food products.

Nucleating agents

In industrial applications, nucleating agents are commonly added to accelerate the crystallisation rate, reduce processing cycle time, and improve physicochemical characteristics such as optical, mechanical, and heat resistance properties (Zhou et al., 2007; Tang et al., 2004). Commonly used nucleating agents are organic and inorganic small molecules, i.e. metallic salts of aliphatic or aromatic carboxylic acids, metallic salts of aromatic
phosphorus compounds, quinacridones, pigments, and minerals such as clay or talc (Mohmeyer et al., 2007).

Polymers with a medium crystal growth rate, such as polyamide 6, polypropylene, and polyethylene terephthalate, can obviously be more strongly super cooled than the rapidly crystallising polyethylene, and for this reason respond very well to heterogeneous and a thermal nucleation with the aid of foreign substances -- the nucleating agents. Conventional processing of polymers such as polystyrene and polycarbonate, having a very low crystal growth rate, always results in an amorphous form. The number and size of the spherulites formed are determined by whether the nucleus formation is homogeneous or heterogeneous. Since many nuclei are formed in the presence of a nucleating agent, under the same cooling conditions the resulting spherulites will be considerably smaller than in a material to which no nucleating agents have been added. Nucleated polymers therefore have finer grain structures than unnucleated ones, and this is reflected in their physicochemical characteristics; thus, coarse-spherulitic plastics are more brittle and less transparent or translucent than ones with the same crystalline fraction but a fine-spherulitic structure (Zhang and Xin, 2007). So-called spontaneous nucleation, i.e. nucleation without an intentional introduction of a nucleating agent, is generally believed to be due to foreign substances such as catalyst residues, oxidatively degraded polymer. Spontaneous nucleation should be distinguished from autonucleation, in which the crystallisation is triggered by incompletely melted down crystallites of the polymer. Nucleating agents raise crystallisation temperature and speed of semi-crystalline polymers by changing their morphology (Nagarajan et al., 2000; Blomenhofer et al., 2005). This results in an increase of thermal conductivity, which leads to faster cooling of the plastic parts resulting in substantial increase in productivity. Other potential benefits are improvement in optical clarity of translucent resins (such as polypropylene) and in some cases increase of the mechanical strength of the material is also achieved (Dong et al., 2007). The effect of nucleating agent on the crystalline morphology under different structure levels of polypropylene materials was investigated by Xu et al. (2003). From their analysis, increase in levels of nucleating agent has an effect on both high and low levels of the crystalline structure. They also observed that nucleating agent showed a heterogeneous nucleation effect. Also, the results showed that at the level of the aggregation structure, crystallinity increases and spherulite size tends to decline with increase in nucleating agent. At the same time, the nucleating agent also has an effect on both the crystal grain structure and the unit cell structure.

In another study by Li et al. (2010), the \( \gamma \)-cyclodextrin (\( \gamma \)-CD) inclusion complexes (ICs) with four kinds of polyolefin (PO) as guest molecules showed that the crystallisation behaviour of isotactic polypropylene (iPP) blended with the \( \gamma \)-CD and \( \gamma \)-CD-PO ICs exhibited highest crystallisation temperature (TC), smaller spherulites, and faster crystallisation rate than those of neat iPP. This indicates that the ICs play a role of nucleating agent on the crystallisation of iPP and induce accelerated crystallisation. The IC with PO, having higher TC as guest molecules, showed higher nucleation effect than the IC with PO TC as guest molecules. Their results suggest that the nucleation effect of these ICs was affected by the kinds of the guest molecules. The higher TC guest molecules could result in higher nucleation effect.

Despite the availability of comprehensive literature on the nucleation of polypropylene, its commercial application is relatively recent. Industrial applications are the most relevant and its use as nucleating agents in the processing of slowly nucleating and crystallising bulk polymer isotactic polypropylene (i-PP) has been well documented. It can be anticipated that the advances in the development of multifunctional additives for tailoring physicochemical properties for other polymers is needed for wide applications. In addition, these additives should exhibit excellent thermal stability, and do not feature absorption of visible light, adding to a most favourable set of characteristics that can provide marked benefits over presently employed nucleating/clarifying agents.

Light stabilisers

Light stabilisers are chemical compounds capable of interfering with the physical and chemical processes of light-induced reactions. Light stabilisers are among the most expensive plastics additives in use and have global market of $530 million, which represents about 60-65 million pounds. With annual market inflation of 6-7 per cent, they are among the fastest growing plastic additives (Murphy, 1996). This is mostly because they help the coattails of polypropylene, perhaps the fastest growing commodity polymer. Ultraviolet (UV) stabilisers are somewhat in fashion, however, from a technical point of view and the most important light stabiliser classes used are: 2-hydroxybenzophenones, 2-hydroxyphenyl benzotriazoles, hindered amines and organic nickel compounds along with salicylates, cinnamate derivatives, resorcinol monobenzoates, oxanilides, and p-hydroxybenzoates. The sterically hindered amines (HALS) represent the latest development in this field. Light stabilisers are generally used in concentrations between 0.05 and 2 per cent, the upper limit of this range being employed exceptionally. Among other factors, the concentration used is a function of the inherent light stability of the resin to be stabilised, for the specific application under consideration, and of the other additives in the formulations, e.g. antioxidants, pigments and fillers. UV light blockers/stabilisers are often used in clear or tinted packaging to protect personal care, food, and beverage products from UV light degradation coming from sunlight or in-store fluorescent lighting (Murphy, 2001; Pritchard, 2005). UV light can degrade not only the colour but also the flavour and nutritional value of beverages packaged in clear PET bottles. Fruit juices, tea, and sports drinks are particularly susceptible. As clear and transparent packaging materials gain more popularity and use, protecting products from UV damage becomes of critical importance. Ciba® Shellflus® UV 1100 blocks 90 per cent of UV light up to 390 nm. Recently introduced Techspere™ PTM 12125P UV light blocker for PET is specially formulated to minimise haze when processed at less than 288°C (550°F). ColorMatrix is commercializing new UV blocking chemistries for PET bottles and films. The new chemistry is much stronger, blocking UV light over 390 nm, compared to the typical benzotriazole chemistry that blocks effectively up to 370-380 nm. The technology is significantly less expensive and does not impart colour.

For practical stabilisation, it is important to distinguish between stabilisation through the UV absorption mechanism and stabilisation by other mechanisms. Among the light stabilisers classes available commercially today, only a few may be used in a broad range of plastics. Thus, nickel compounds are used almost exclusively in polyolefins whereas polyvinyl chloride, e.g. is usually stabilised with UV absorbers. This has put forth a challenge before polymer chemists to broaden the range of light stabilisers for the food and drink industry.
Blowing agents
Since the production of foams began, more than a thousand compounds have been investigated as chemical blowing agents and most of them described in the patent literature. Chemical blowing agents (CBA) are additives, which are able to evolve gas through chemical reactions and produce foam structures in a polymeric matrix (Ram, 1997). In the majority of cases, the gas is evolved at elevated temperatures by thermal decomposition of organic or inorganic compounds. There are two kinds of blowing agents, i.e. endothermic and exothermic. In a few blowing agent formulations, the blowing gas is released by the endothermic reaction of two components (Singh, 2001). The primary criterion governing the choice of a blowing agent for expanding a particular plastic is its decomposition temperature. The blowing gas must be evolved within a defined temperature range, which includes the processing temperature of the plastic concerned. The blowing agent must not be decomposed too spontaneously, as in the case of an explosive; otherwise heat build-up and combustion could occur due to the heat generated by the exothermic reaction. The gas formed should preferably consist of nitrogen or CO₂ and should not contain explosive constituents. The blowing agent should be easy to incorporate and to disperse evenly in the plastic concerned (Murphy, 1996). CBAs are used in plastics for a variety of reasons: weight reduction of the parts, removal of the sink marks and for nucleation in direct gassing. While stable at ambient temperature, CBAs decompose during processing and yield significant amounts of gases and small amounts of solid residue. Different applications call for different classes of CBAs. There is increasing interest in expanded thermoplastics with higher heat deflection temperature (engineered plastics), such as polycarbonate and liquid crystal polymers. Virtually all known thermoplastics can be expanded using the chemical blowing agents currently available. The primary consideration of development work is the modification of known compounds with the aim of achieving the properties of an ideal chemical blowing agent. Azodicarbonamide type CBA provides vigorous foaming action and are frequently the most economical but is now banned for food packaging applications. Endothermic CBAs allow the best control over decomposition rates, and better quality of the parts. In some cases, combination of the two types gives the best results (Pritchard, 2005). There are other classes of CBAs, but they are not used as frequently as those mentioned previously.

Expanded plastics have been around for over 50 years. Expanded plastic articles made from the “commodity” plastics PVC, PE and PS are firmly established in their fields of application and it is hard to imagine the market without them. Virtually all known thermoplastics can be expanded using the currently available chemical blowing agents. The probability of new chemical blowing agents is low; however, high-temperature blowing agents may be the only new products of future.

Plasticisers
A plasticiser is a substance, which is added to a material (usually a plastic, resin or elastomer) to improve its processability, flexibility and extensibility. A plasticiser can decrease melt viscosity, glass transition temperature and the modulus of elasticity of the product without altering the fundamental chemical character of the plasticised material. Polymeric plasticisers (usually polyesters, based on adipic acid) extend the life of PVC end-products considerably. They slow down migration, extraction and volatility (Wilson, 1995). Although, molecular weight has a significant influence on performance but other factors also determine polymer characteristics. Demands made on ecological and toxicological performance, including those made by contact with food or body fluids are becoming increasingly stringent. Because of this, low volatile plasticisers such as diisononyl, diisodecyl, nonyl undecyl and diundecyl phthalates as well as certain trimellitates, which are also highly extraction resistant, will become more important in area of food packaging. Apart from these plasticisers, amides and hydroxylamine are also used in the processing of soy protein plastics (Liu et al., 2007; Tian et al., 2009). Those plastics, which come into contact with food, lubricating oils and fuels, the use of polyester plasticisers will become almost mandatory. In medical and food technology, plasticisers, which have undergone detailed toxicological investigations and of highest purity will maintain their place.

Esters of fatty acids and monocarboxylic acids
Can be used as viscosity depressants for PVC pastes and also as secondary plasticisers for plasticised PVC compounds. They are in liquid form and advice should be sought on food contact approval. Starch acid esters are used as plasticisers and processing agents for various plastics as well as lubricants for polystyrene. They are semi-solid and have general food contact approval.

Sebacates and adipates
Provide good low temperature plasticisers for PVC, in liquid form, with fairly general food contact approval. Di-butyl sebacate is a highly efficient primary plasticiser for low temperature applications used in films and containers for packaging.

Epoxidised grades (soya bean oil, linseed oil)
Used as stabilising plasticisers with properties of migration resistance, in PVC compounds, alkyl resins and chlorinated paraffins, and as pigment dispersing agents in plasticised PVC. Alkyl epoxy stearate plasticisers are used as low viscosity stabilisers, especially in PVC pastes, with some grades providing low temperature properties. They are in liquid form. Soya bean versions have widespread approval for food contact.

Widespread use of plasticisers in food contact and medical applications are among the most extensively studied substances around in relation to health and safety. The plasticisers used for food packaging applications have the approval of the Food and Drug Administration (FDA) and Environmental Protection Agency (EPA) in the USA as well as European food safety authorities. Low volatility and non toxicity will be high priorities, which can be focussed in further research and development. The requirement to reduce odour during processing with organotin mercaptides will be a field of further activity on ecological ground.

Antifogs
The formation of “fog” on plastic film or sheet is the result of the condensation of water vapour on the surface of transparent sheet or film. This physical condition may be the result of a number of things:

- The temperature of the film surface on the inside falls below the dew-point temperature of the air and water vapour that is within the headspace of the article.
- Air near the film’s surface cools to a temperature at which it cannot retain all the water vapour; as a result, excess water condenses on the film’s surface.

This effect is based on the relationship between the temperature of enclosed air, the relative humidity of the air, and dew-point
temperature (De Ell et al., 2003). The difference between the surface tension of the condensed water and the critical wetting tension of the film’s surface is crucial in packaging applications. When this packaged item is stored in a cool environment, the moisture condenses on the surface causing fog to appear on film surface. Depending upon the application, this fog is typically not considered aesthetically pleasing and may increase food spoilage (Hobson and Burton, 1989). There are two routes the packaging industry uses to minimise the formation of fog on sheet, film, or thermoformed articles: internal additives or external topical coatings (Gorny and Brandenburg, 2003). The functionality of antifog technologies is accomplished by coating the interior surface of the flexible packaging material with compounds that reduce water surface tension or reduce the ability of the water to adhere to the packaging material and thus cause the condensed water to run off the interior surface of the package.

**Internal additives**

Internal antifog additives are generally non-ionic surfactants. These additives are added at the film production stage mainly in the form of concentrates or master batches. These additives usually have a certain level of incompatibility with the blended polymer matrix, resulting in their surface migration. The internal agents have a level of durability over time with regard to maintaining the antifog performance since there is a source of the agent in the polymer, which has a chance to replenish the surface through migration effects over time. These additives usually are surface activators, which reduce the surface tension of the water droplets that may form on the film’s surface due to condensation. As a result, the surface tension between the water and the substrate surface is reduced. This reduces the contact angle of the water molecules, and the water is able to spread out more creating a more uniform layer. This effect helps to improve the transparency of the water droplets on the film’s surface and minimises any lens effects. There are many commercially available internal antifog agents for polyolefin systems, but they are limited for polyester systems. This is because polyolefin is more hydrophobic and typically exhibit surface tensions around 30 dynes/cm versus polyester that is around 40-44 dynes/cm. The hydrophobic nature of polyolefin allows for a broad selection of agents, many of which are incompatible and readily migrate to the surface. Polymers, however, are more polar and typically have a better level of compatibility with the antifog additives.

**External topical coatings**

Coatings can be applied to the surface of the plastic sheet or film. These agents are like internal additives, which are designed to help wet out the substrate’s surface, which decreases the contact angle of the water droplets and improves transparency. These agents are usually supplied as viscous liquids, which are then diluted with water. The liquid is coated to the surface of the sheet or film, either by a dip coating and roller process or by spray application. The sheet is typically dried to evaporate the water and help cure the coating to the surface. External coatings are more commonly used for PET in comparison to internal agents. This is due to the compatibility issue of PET, which has too good internal agents (the compatibility being, which prevents migration to the surface) and also because of the high processing temperatures for PET, which may degrade, the additives during melt extrusion.

In fresh-cut produce packaging, antifogs prevent the film from fogging so that the consumer can see the product clearly. Temperatures recycling of high equilibrium relative humidity foods have led most film manufacturers to offer heat seal plastics with an antifog additive. The additives are chosen for their amphiphilic nature, with the nonpolar chain in the plastic and the polar end group at the interface. The use of antifogs in fresh food packaging is on the increase and will continue in the future as new applications as well as new polymer entrants into the fresh food packaging industry continue to evolve (Barmore, 1987). Antifogs act as a surfactant, so that moisture given off by produce forms a transparent, continuous film on the package surface rather than forming beads of water. Although the preferred polymers used to absorb the water are polyacrylate salts, graft copolymers of starch can also be used. The inter chain bonds between the polysaccharide chains are disrupted, allowing the starch to absorb the water by hydrogen bonding. Such polymers tend to become slimy when swollen with large amounts of water. The swelling of the polymer on hydration results in substantial distortion of the duplex sheet, an effect that is controlled somewhat by the quilted seal pattern. A new trend towards microwaving of fresh-cut produce packages, such as spinach products, has led to challenges of meeting performance requirements and regulatory requirements, which are stricter at elevated temperatures. For example, the Cryovac® microwaveable vegetable bag has an antifog coating, which also aids in improving the shelf life of the vegetables. The extended shelf life is due in part to the permeability of the package, but also to the “synergistic effect” of the antifog coating that reduces moisture, which can encourage the growth of spoilage bacteria. Commercial products available for compounding include Ciba’s Atmer™ 7000/8000 series of antifog pellet concentrates and Techmer PM’s Techspere™ antifog additive. The marketing departments of the most important companies in the field of foodstuffs are more and more devoting themselves to the research and development of new packaging solutions to give a better presentation of foodstuff to customers. Frilvan® has recently prepared a new line of food-grade antifog master batches for the production of film directed to the packaging of foodstuffs to preserve the see-through effect despite the presence of humidity inside the package (as ready-to-use salad, so that the customer is enabled to see the product inside the package). The wide range of these master batches as well as their formulations to split up the applications by: packaging in cold environment (film for packaging of ready-to-use salad for sales in supermarkets); and packaging in hot environment (packaging of delicatessen products such as spit roasted chicken).

Desiccants are also sometimes referred as antifogs, which can be coextruded in-between layers of resin for moisture control. This process is accomplished by using a co-extrusion head on the moulding machine to create a multilayer wall in the package. For example, TricorBraun (St Louis, Missouri) has developed a DryKeep™ blend made with magnesium sulphate and HDPE/LDPE to create a blow moulded resin. Benefits of having a desiccant in the layers of the packaging are that it can absorb moisture from inside or outside the bottle (Markarian, 2006).

The use of antifogs in fresh food packaging is on the rise and will continue in the future as new applications along with new polymer entrants into the fresh food packaging industry continue to evolve. Antifogs can be impregnated into the film as an additive or applied as a liquid coating.

**Masterbatch additives**

A Masterbatch is defined as “a highly concentrated colour and/or additive system contained in a resin matrix for
addition, at low levels, to uncoloured resin during extrusion”. Masterbatches consist of colorants, additives and a plastic carrier material. Universal masterbatches utilise carrier resins like waxes, polyethylene or ethylene vinyl acetate copolymer (EVA), which can be mixed with several thermoplastic materials. Additives are used in order to achieve technical effects in plastic materials. Additives may be implemented in separate masterbatches or in multifunctional masterbatches that contain both colorants and additives (Murphy, 1996). The additive could help food companies to keep odours within a package or prevent outside ones from affecting their products. The additive can be used in low-density polyethylene (LDPE), linear LDPE and ethylene vinyl acetate films used for food packaging. The active ingredient in Ampacet 10178™ is highly porous and preferentially adsorbs smaller, odour-causing molecules, especially polar and ammonium based compounds. Masterbatch additive for development of moisture regulating films for packaging of fresh foods has been successfully formulated at our laboratory (unpublished results). These packages keep the food fresh for longer time with all sensorial characteristics intact and enhance the appearance of the package, which satisfies the consumer’s demands for fresh foods. Employing innovative masterbatch formulation techniques and focus on processing aids, lubricant packages will be the main theme in masterbatch additives research. Contributing to the success of the masterbatch is the fact that grades can be tailored to suit individual manufacturing processes. Looking ahead, the development of a new range of additive package formulations that include antimicrobial, UV, antistatic, process aids, and specific problem-solver characteristics will continue.

Legislations/regulatory aspects

The Federal Food, Drug and Cosmetic Act of 1938 (FFDCA) authorize FDA to regulate food additives. FDA approval of a food additive is not limited to a single sponsor, but is generic in that anyone can manufacture or use an additive consistent with any existing patent protection. In regulating food additives, FDA classifies the additives into four categories:

1. Prior-sanctioned substances, which were approved either by FDA or the US Department of Agriculture (USDA) before the passage of the 1958 Food Additives Amendments.
2. GRAS additives (generally-recognized-as-safe) which are exempted from regulation because their extensive use has not produced any harmful effects.
3. Direct additives which are intentionally added to foods such as lemon flavouring in cookies.
4. Indirect additives which are often trace substances that leach from packaging materials and migrate to food during processing or storage.

In Australia, State Food Act controls the possibilities of such migration by general provisions governing the sale of food: they contain provisions that no person shall sell any article which is adulterated or falsely described, which contains any matter foreign to the nature of the food or which is packed or enclosed for sale in any manner contrary to any provision of the Act or the Regulations. The Australian Food Standards Code, which complements the Food Acts, sets maximum migration levels for three specific monomers, the “building blocks” of plastics. These are vinyl chloride, acrylonitrile and vinylidene chloride. They are singled out for special attention because of their known potential toxicity. Modern manufacturing methods have reduced monomer residues in food contact plastics to the point where they are no longer measurable. Numerous other packaging materials are used in contact with food including paper, fibreboard, glass, tinplate, aluminium and various types of plastics. Australian Standards (apart from food regulations) are used to define compositional requirements of a number of plastics for food contact applications. However, these standards cover only six of the common plastics used in food packages and refer to the additives which may be used in their manufacture rather than setting limits on migration. The selection and control of these additives has been based on what is permitted in some overseas legislation. Both the US and the European Community either have, or are preparing, complex regulations to control migration from food packaging materials. In some instances, these regulations set maximum limits for potentially harmful migrating substances. In other cases where migration presents a minimal hazard, permitted additives may be listed without specific limits being set. Some plastics contain a large number of additives including antioxidants, stabilisers, antistatics and plasticisers. These are included to improve the functional properties of the plastics.

Conclusions

Many of the additives discussed are used in combinations with each other to optimise performance and create specialised polymer blends. Many technological advances that have occurred over the years have revolutionized both the polymer and packaging industries. The ability to modify polymer properties enables new materials to be utilized to improve performance, efficiency, and the protection of packages. As consumers demand improved product quality and longer shelf life, there is a continuing need for improved barrier properties in packaging for food and beverages, cosmetics, and pharmaceuticals. Additives that help to create a protective package environment, polymers with good barrier properties, and processes for creating modified atmosphere packaging (MAP) and sensors to measure the package environment can be combined to achieve the wide array of packaging materials. Within the next decade, active and intelligent packaging options involving use of additives in packaging materials/packages will become key elements in how food processors and manufacturers protect the longevity and nutrient value of their products. While many active packaging technologies such as desiccants, odour scavengers and ethylene absorbers are commonly used in sachets, which can be inserted into a package; there should be a drive to find ways to incorporate active packaging technologies directly into the package walls.

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Pigment & Resin Technology

Volume 41 · Number 6 · 2012 · 368–379

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