Impact Objectives

- Develop oxidatively degradable polymeric materials
- Explore the potential of diacylhydrazine in the form of a novel, environmentally-friendly polymer

A fantastic plastic

***Professor Nobuhiro Kihara** shares some insights into the tough and stable plastic he has developed that can be easily dissolved when finished with, and its potential applications*

Can you begin by introducing the polymer you developed?

The key feature of the polymer we developed is its all-or-nothing degradation behaviour. The polymer is very tough and stable during use, but when we decide to finish using it, we apply sodium hypochlorite solution (which is easily available in drugstores as bleach) as the signal of end-of-use, and it degrades rapidly, dissolving in the solution.

How are you progressing with your work to develop oxidatively degradable polymeric materials?

There are two types of oxidant: one is the oxygen in the air, and the other is chemicals such as bleach. Interestingly, their reactivities are completely different and another distinction is their locations: oxygen is present anywhere, while chemicals are always in a bottle. We use chemicals only when we want to.

We have developed a new type of plastic, in which a special switch is installed. This switch is non-responsive to most stimuli such as heat, photoirradiation, water, acid and air (which includes oxygen), but is very sensitive to bleach and related chemicals. Given the very different reactivities of oxygen and chemicals, this plastic is robust during use even at high temperatures, in wet environments, under sunlight, with acid and in air (that is in oxygen). But it rapidly decomposes in bleach; dissolving in the solution. The decomposition products are generally safe, and the solution can be poured down the sink.

Because there is no oxidant in the room except in the air (but it is oxygen) and in the bottle of bleach, you can trust the stability of this plastic during use. But, once you finish using the plastic, you can use the bleach to dissolve it. There are many possible applications for this. For example, adhesives can be removed without a trace, paint can be removed to expose the surface underneath and used nappies can be dissolved in the toilet.

What are some of the methods and tools you are using in your work?

The only special tool in this particular investigation is hydrazine. Hydrazine is the simplest diamine. There are several diamine-based classical polymers such as polyamide. Using hydrazine instead of conventional diamine, produces an oxidatively degradable polymer. Or an oxidatively degradable polymer can be obtained by copolymerising hydrazine in the conventional condensation polymerisation system. Hydrazine has an N-N bond. When a hydrazine derivative is oxidised, the N-N bond is oxidised to N_2 gas, and is kicked out from the molecule to break the main chain.

From your perspective, why is this research so important?

To solve the problem of plastic waste, much attention has been focused on degradable polymers. Among various degradable polymers, the most attention was paid to biodegradable polymers because the other degradable polymers such as photodegradable and thermodegradable polymers are unstable in ambient circumstances. However, even biodegradable polymers are degradable during use via rot or mould, as well as biomaterial such as wood and paper. That is why biodegradable polymers are not suitable in dietary, sanitary, medical and related applications. Biodegradable polymers are useful only for applications where the plastic material is placed in the field and will never be collected back. For example, ground sheets for agriculture should be made of biodegradable polymers. However, if the plastic material is disposed of in the bin after use (as you do), or if the plastic products are collected after use, it is not necessary to be biodegradable. Moreover, if a plastic material is made of biodegradable polymer, people may start disposing of plastic waste outside of the bin. This situation is very serious.

The oxidative degradation of the powder of polydiacylhydrazine. The bubble is nitrogen gas evolved during decomposition

The perfect polymer?

Researchers in the ***Department of Chemistry*** *at* ***Kanagawa University*** *are exploring the exciting potential of diacylhydrazine in the form of a novel, environmentally-friendly polymer*

Polymers have diverse properties and as such have a range of applications in everyday life. For example, they are a key component of plastics, which are ubiquitous materials and are also used in industries such as textiles, packaging, construction and aircraft. One of the things that makes polymers so useful is that their structure can be altered to produce the desired material. For instance, acrylic is an example of a thermoforming polymer, which can be reheated and reshaped, while biodegradable polymers have medical and agricultural uses that are possible due to their ability to break down following its use. There are also polymers that are stable and maintain mechanical strength even under extreme conditions, known as engineering plastics. With polymers being so useful, they are increasingly prolific and therefore their improper disposal is a growing problem.

Diacylhydrazine is a functional group that is thermally and chemically stable. It can be incorporated into polymers to promote thermal and chemical stability and, what is more, may make them oxidatively degradable. Oxidatively degradable polymer can be disposed of easily, safely and in an environmentally-sound way after use. This is at the heart of the current research of Professor Nobuhiro Kihara at the Department of Chemistry, Kanagawa University in Japan,

POLY(DIACYLHYDRAZINE)

Recognising the need for a polymer that has a degradation reaction initiated by artificial stimuli, Kihara is interested in the novel concept of oxidatively degradable polymers. In fact, Kihara said the research team is the only group studying such polymers. With a background in chemistry, including experimenting on the synthesis of polymers using carbon dioxide, he has been led to diacylhydrazine and its immense potential. 'As the exercise for head-to-head poly(carbon dioxide), I prepared nylon-0,2, which is the most simple poly(diacylhydrazine) and is expected to be derived to the nitrogen analogue of head-to-head poly(carbon dioxide) after oxidation. Nylon-0,2 was a thermally and chemically very stable polymer. However, when it was oxidised, nothing was obtained, and the only products were nitrogen and carbon dioxide gases,' explains Kihara. 'At that time, I understood I had found the key structure, diacylhydrazine, for a novel degradable polymer that is stable during use, and is highly degradable after use,' he says.

Using diacylhydrazine, the researchers have developed a novel polymer with attractive properties as well as vast benefits and potential applications. The polymer can be used in plastic, adhesive or paint, with further possible uses. Despite its thermal and chemical stability, diacylhydrazine can be degraded easily and quickly using an oxidising agent such as bleach. 'Our degradable polymer is inert to ambient stimuli and keeps high strength, although it rapidly degrades when we decide to start degradation,' Kihara describes. In addition to thermal stability and chemical resistance, the polymer the researchers have developed also demonstrates weather resistance, and will not be decomposed by heat, water, acid or sunlight. A key benefit is that this polymer can be disposed of easily and conveniently after use. 'You can remove the specific polymer, which can be the adhesive or paint, from the substance at your desired instance. The remover is bleach that can be found in supermarkets. Furthermore, there are no negative consequences for the environment,' confirms Kihara. 'If adhesive, paint and plastic pieces are made of this polymer, they can be removed as we desire. If a composite is constructed using this polymer, we can easily separate it to the elements. Therefore, the recycling or reuse of the materials will be easy with this polymer,' he outlines.

FURTHER POLYMER POTENTIAL

The polymer has huge potential with the ability to be reused or recycled as desired and could be a game changer. 'Oxidative

degradation will reduce the load for the disposal of plastic. A composite can be separated to the raw materials, which can be recycled easily,' highlights Kihara. 'After paint is removed to retrieve the clean surface, the material can be reused anywhere. The robust degradable polymer will change the concept of how to use the polymeric materials,' he says. There are further possibilities, with diacylhydrazine being just the tip of the iceberg. 'Poly(diacylhydrazine) is merely an example of oxidatively degradable polymers. There can be various oxidant-induced degradation reactions that can be used for the design of degradable polymers,' states Kihara. There may also be ways other than oxidation to initiate degradation. 'Artificial stimuli other than oxidation, for example, electric current, may also be developed for the degradable polymer,' he says.

> *Our degradable polymer is inert to ambient stimuli and keeps high strength, although it rapidly degrades when we decide to start degradation*

In their studies, the researchers measure the strength and toughness of the polymer using standard methods and are able to easily see oxidative degradation due to change of appearance or by using chromatography. 'Most of them dissolve in sodium hypochlorite solution with the evolution of nitrogen gas via oxidative degradation. Some polymers do not dissolve, but tough polymers become fragile,' explains Kihara. 'If the appearance does not change, we can monitor the degradation by chromatography that is used to estimate the molecular weight of the polymer,' he outlines.

FINDINGS AND COLLABORATIONS

Kihara and the team have unearthed a number of exciting findings to date. These include the development of oxidatively degradable epoxy resin that can be used as an adhesive, as well as an oxidatively degradable SAP (superabsorbent polymer). 'The swelled oxidatively degradable SAP dissolved in water within a few seconds after the addition of sodium hypochlorite solution and the product is poly(acrylic acid), which can be flushed down the toilet,' Kihara describes. Furthermore, the researchers have developed a CFRP (carbon fibre reinforced plastic) where the matrix polymer is oxidatively degradable. 'We prepared a CFRP plate with an oxidatively degradable matrix using a carbon fibre sheet. When it was treated with sodium hypochlorite solution, the matrix polymer was dissolved, and the carbon fibre sheet was directly recovered without any damage,' he reveals. What is more, it would be possible for the researchers to use the recovered carbon fibre sheet to prepare a new CFRP plate.

The researchers have established important collaborations that have assisted their progress but are looking to expand on these to allow their research to reach its full potential. 'We have some collaborations with companies, but not with an institution. Most companies have interest in the oxidatively degradable epoxy resin that can be used as the adhesive. When we hear how researchers in institutions or industries are interested in the oxidatively degradable polymer, we learn important new concepts and ideas and, in order to meet certain requests, have even developed new chemistry. Collaboration can be considered the driving force of our research,' highlights Kihara.

Looking ahead, he would like to collaborate with more companies in order to translate his polymer, which is a raw material, into real-world applications. In the future, Kihara and the team would like to focus on the oxidative degradation of diacylhydrazine without using sodium hypochlorite solution, introducing the diacylhydrazine moiety into the main chain of vinyl polymers and investing a different oxidatively degradable functional group.

Project Insights

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BIO

Professor Nobuhiro Kihara studied at The University of Tokyo and then worked at the Research Institute of Resources Utilization at Tokyo Institute of Technology on the reaction of carbon dioxide with epoxide and the application of the resulting cyclic carbonate. He was a postdoctoral fellow at Fribourg University, Swiss, and worked as an Associate Professor at Osaka Prefecture University. Kihara moved to Kanagawa University as a professor in 2005. His present research interest is on polycatenane, artificial molecular motors, the reaction field based on molecular recognition, the chemistry of heteroatom-heteroatom bonds and the oxidatively degradable polymer.