Review

Self-repairing mechanism of plastics

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Abstract

The protection mechanism of a living body and man-made materials can be classified into two categories. One is a passive protection by which the body and materials are guarded by simple chemicals such as light absorbents, and the other is an active protection that repairs with metabolic reactions the internal injury suffered by many kinds of deterioration factors from the outside. Polyphenylene–ether was selected as a man-made material in which the metabolic reaction can be achieved in the atmosphere (21\% of oxygen) and at room temperature (20–40 °C). The polymer introduces oxygen as an energy source, transports it with copper-complex and repairs the scission point of the chain. Such active protections were attempted for several polymers and some advantages and problems were elucidated. In this paper, the mechanisms of active protections in some plastics are reviewed and are also compared with protection systems of a living body, which provide us with very useful information on the development of advanced materials.

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1. Introduction

Many works on the survey, preparation, and the analysis of man-made materials that mimic the living body and their application to various complexes have been conducted in the fields of chemistry, materials science, mechanical engineering and other scientific fields for decades [1,2]. In particular, studies on the bio-membrane have produced excellent results in which the concept of active transportation has been elucidated [3–6]. The bio-tissues in bone, skin, muscle and others have also been researched closely and some ‘bio-mimetic materials’ have been artificially prepared [7]. These materials have been applied to artificial blood vessels, bone, organs, and other materials in regeneration medicine. Various reactions and catalysts in a living body have also been studied to apply them to artificial systems [8,9]. The individual papers on advanced materials and their application mentioned above are not referred to in this paper because excellent reviews on the subject can be easily obtained and related symposiums are held in various places in the world [10,11].
The subject of this paper is the application of the metabolic system in a living body on man-made materials and the development of self-repairing materials with/without metabolism. Another interest is the difference in information exchange, signal transduction and data transmission from the database to materials and systems between a living body and man-made materials. The experimental data and the review of the former will be summarized and the latter will be discussed in this paper.

2. Self-repairing materials and their system

2.1. Short review on self-repairing materials and their system

The concept of man-made self-repairing materials has been discussed for several decades and many efforts have been made to prepare advanced materials, systems and equipments that have self-repairing abilities [12,13]. White, Brown and their colleagues published their works on automatically healing polymer and self-repairing polymer. When a crack is generated in the resin, the microcapsule that has been blended prior to the fabrication is destroyed [14]. The cyclopentadiene in the capsule is infiltrated into the matrix and is polymerized by the ruthenium catalyst that has also been blended into the polymer. Although the structure of the repaired polymer is different from the original one, the mechanical strength can be recovered by 75%. Brown and his co-workers showed 'the epoxy matrix composite incorporating a microencapsulated healing agent that is released upon crack intrusion' [15]. The composites of epoxy resin [16] and hollow fiber [17] were reported as self-repairing plastics.

Adding the fine particles of epoxy resin to GFRP (glass fiber reinforced plastics) is one of the typical methods. The crack is reported to be patched by heating for 5 min at 110 °C and 90% of the flexural strength recovers [18–20]. The microcapsule method is also applied to concrete materials. The capsule automatically melts and releases the anti-catalyst to the setting. It can prevent hydration that leads to the fracture of the concrete by rapidly increasing the temperature [21,22].

Mullite composed with Al2O3 and SiO2 and SiC as the supplementary agents are added to ceramics. One hundred and twenty five percentage of the mechanical strength of the materials recovers after crack generation by holding for 1 h at 1300 °C. SiO2 and Y2Si2O7 are generated in the crack and they repair it by the oxidation reaction [23,24]. The retardation of creep propagation has been studied by Kyono et al. to maintain the strength of metals such as 304BNTi stainless steel which contains B, N, Ce and Ti (19Cr–10Ni–Ti, B, N, Ce) [25,26]. They claimed that the creep propagation could be controlled by the segregation of sulfur and BN coating. These are listed in Table 1.

The above works have an inclination to focus on the healing of cracks or the restoration of tensile strength or other characteristics. They make full use of all efforts by which the basic phenomena and the healing of chemical deteriorations and fracture phenomena have been clarified [27,28]. On the other hand, these cracks and the decrease in strength are due to the structural change of atoms or molecules. Therefore, the inverse reaction of the chemical deterioration and the putting the same kinds of atom or molecule back in their inherent sites will be one of the repairing methods. This paper does not focus on cracks or macroscopic characteristics but on 'nanoscopic' deterioration.

Generally speaking, polymer chains are damaged by heat, light and external mechanical force, and the reactions are irreversible. This is one of the reasons why no repairing agents are used for industrial materials but many protection additives such as anti-oxidation, anti-ultraviolet, and heat-resistant agents are applied to retard the damage [29,30]. As for external mechanical force, the initial design of the polymer has hitherto been ‘overdesigned,’ taking the deterioration factor into account because no additives for protection have been discovered.

The concept and the classification of the deterioration factors and the protection systems will be defined and described here prior to the reviewing of self-repairing systems. The causes of deterioration are: (1) harmful materials and living bodies such as oxygen, oxidizing agents, poisons, active materials, virus, bacteria and others, (2) factors from the surroundings such as heat, visible light, external mechanical force, radiation, pressure and others, and (3) attack by various factors such as strong wind, rain,

| Materials       | Key additives                        | Effects                                    | Key factor to control repair |
|-----------------|--------------------------------------|--------------------------------------------|-----------------------------|
| Matrix          | Agent                                | Catalyst                                  | Amount of chemicals         |
| Polymer         | Epoxy resin                          | Cyclopentadiene                           | Amount of supplementary     |
| Cermics         | Silicon nitride                      | Supplementary agents                      | agents                      |
| Cement          | Concrete particle                    | Sement particle                           | Amount of sement particle   |
| Metal Composite | 304BNTi                              | B, N, Ce, Ti                              | Amount of B and N           |
|                 | GFRP                                 | Resin powder                              | Amount of resin powder      |

Table 1
Examples of self-repairing materials
insects, collapse of the adjacent structure, a sudden blow with a rod, human beings and others. As there are many causes as listed above, they will be called ‘DF’ (deterioration factor) for short in this paper.

The protection system can be classified into two categories. One is ‘passive protection’ and the other is ‘active protection’. In the former case, the DF directly attacks the protection additives in place of the atoms or the molecules composing the materials. This is the main role of the passive protection additive like a pillbox or a fort.

On the other hand, the DF directly attacks structural atoms or molecules in place of the repairing agent in the latter case. In the absence of passive protection additives, the materials with added active protection reagents have high breakage susceptibility. When the concentration of the damaged site becomes high enough to react with the repairing agent, it repairs the damaged site. The characteristics of two kinds of the protection systems are compared in Table 2.

The concentration of the passive protection additive is generally lower because it should directly guard the structural atoms or molecules against DF. On the other hand, the repairing agent in active protection can perform the mission even at low concentration if the agent reacts with the damaged site in a very short time.

The second is the mobility of the agents. The mobility of the protection additive in passive protection is unrelated to defensiveness because the direction and the site of the attack from the surroundings are not fixed beforehand. The repairing agent in active protection can perform the mission even at low concentration if the agent reacts with the damaged site in a very short time.

The third characteristic of active protection is that it must have a ‘memory’ of the inherent structure of the materials, which will be described in the next section.

Both passive and active systems can be recognized in a living body, but only a few types of active protection have been applied to man-made materials. One of the typical examples in a living body is the protection system of trees. A few guard cells in sapwood protect their neighboring cells by active protection. On the other hand, the cells in heartwood are protected by chemical species secreted by the guard cells when they die (after about 10 years). The combination of active and passive protections in a trunk of a tree is the key to the longevity of trees that are composed of vulnerable materials, even under severe circumstances.

### 2.2. Self-repairing materials with inverse reaction

The two types of experiments on active protection will be described in this paper. One is relatively simple and the other is a repairing system accompanied by metabolic reaction.

Polycarbonate (PC; bisphenol-A-polycarbonate), polybutylene-terephthalate (PBT) and polyether-ketone (PEK) were the subjects used to study active protection with a simple reaction. The self-repairing system of each plastic was designed according to the chemical structure of the end group on the main chain. After deterioration treatment, the recovery of molecular weight or mechanical strength was observed [31]. The self-repairing was observed.

PC, as the first example, is one of useful engineering plastics and is generally prepared by using bisphenol-A and phosgene [32]. The chain of PC tends to be cut by heat (thermal degradation) and acid (hydrolysis) to decrease the molecular weight [33–35], which causes severe damage to the mechanical strength [36]. For example, the tensile strength strongly depends on the molecular weight as plotted in Fig. 1. If the viscosity-average molecular weight \( M_v \) becomes less than 20,000 by thermal degradation or hydrolysis, the strength will rapidly drop.

Several kinds of PC were studied in this work, paying attention to the chemical structure of the end group. The standard type of PC in the market is polymerized by bisphenol-A and phosgene. The end groups are phenoxy and isopropyl groups. Several experiments were tried using PC, but the self-repairing attempts were unsuccessful for all of them. Then, different structures of PC were tried and active protection was observed using Na2CO3 as a repairing agent and PC prepared by the ester exchange method. The ends

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| Classification | Passive protection | Active protection |
|---------------|--------------------|-------------------|
| Target        | Protection agents  | Structural atoms  |
| Amount        | Concentration      | or molecules      |
| of protection | that can protect   | Depend on        |
| agents        | deterioration      | repairing rate    |
| Protection    | Contain            | Nothing           |
| Repairability | Nothing            | Contain           |
| Movement      | Needless            | Need              |
| in material   | Needless            | Preferable to     |
| Memory of     |                    | memorize          |

![Fig. 1. Tensile strength as a function of the molecular weight of PC.](image)
were assigned to 30% of phenyl and 70% of the phenoxy group.

One of the typical results is shown in Fig. 2. The tensile strength dropped by the deterioration treatment was recovered by the repairing action. The effect of self-repairing was very clear.

The designed repairing scheme during the repairing action is illustrated in Fig. 3 [37].

The carbonate bond is very easily cut by thermal degradation or hydrolysis. For example, 90% or more of the scission points is the carbonate bond by thermal aging [38–41]. So, the concentration of the phenoxy end increases after deterioration and it reacts with a phenyl end. The reaction is accelerated by weak alkaline like sodium carbonate. This suggests that: (1) the OH on the chain end is substituted by sodium ion, (2) the end attacked a carbonate bond on the end of another chain, (3) phenol is eliminated from the chain, and (4) the scission chain recombines another chain.

Another interesting polymer is polyphenylene-ether (PPE), which has been fully investigated as a typically active protection material with metabolism like a living body [42]. The repairing scheme is shown in Fig. 4 [43].

The polymer chain is cut by heat, light, and external mechanical force to produce a radical on the end of the scission chain in the first step. Subsequently, a hydrogen donor stabilizes the radical. The Cu (II) added beforehand forms a complex with each end of the two different chains and withdraws two electrons from them. The chains combine, eliminating two protons from the ends, and the copper changes from Cu (II) to Cu (I). The deactivated Cu migrates in the polymer and two molecules of Cu (I) react with an oxygen molecule to be oxidized to Cu (II). An oxygen ion reacts with two protons to form a water molecule that goes out from the specimen.

Various experiments were conducted to check the above mechanism. The mobility of the chain was supposed to be one of the key factors in accelerating the self-repairing reaction because the two ends of the PPE chain and copper must encounter at the same time in PPE, which is one of the most rigid plastics. The experimental results show that the recovery rate increases with decreasing initial molecular weight (Fig. 5) and increasing amount of dimethylphthalate (DMP) as a diluent (Fig. 6) [43]. It is considered that the self-repairing reaction depends on the concentration of the chain end and the mobility.

Secondly, the recovery rate was expected to depend on oxygen partial pressure in the surroundings and the result is shown in Fig. 7 [43].

The third and most important data to confirm the reaction scheme is plotted in Fig. 8, where the amount of water emitted from the specimen was proportional to the recovery rate [43].

The reaction of 2,6-dimethylphenol (26DMP) as a monomer of PPE and the structural change of the PPE polymer chain have been studied by many researchers [44, 45]. 26DMP reacts with the end of the PPE chain by Cu-organic ligand complex [46–48] and the PPE chain is known to react with several compounds such as quinine [49]. These known mechanisms, as well as the results of these experiments support the scheme shown in Fig. 4.

2.3. Remarkable phenomena observed in the experiments and further research works required for self-repairing design

Three remarkable points in addition to strength or molecular weight recovery surfaced through the experiments.
The first is that the larger the degree of deterioration, the higher the recovery rate [50]. Three different specimens hydrolysed with acidic steam were prepared and the recovery rate of the molecular weight during the repairing period was measured by GPC (gel permeation chromatography) [37]. The reduction of the molecular weight after 75 h deterioration was 15% (0.85 toward the initial molecular weight), which was larger than that after 25 h as shown in Fig. 9. The recovery during the repairing process was 9%, which was larger than that of the 25 h specimen. Such tendency has rarely been observed in the passive protection system where the deterioration rate of the damaged site tended to accelerate. It could be applied to sophisticated industrial goods in order to improve their reliability.

The second is antagonism between deterioration and repairing. The change of the molecular weight of PC is plotted in Fig. 10 as a function of sodium carbonate concentration. The changing rate of weight average has the maximum value at the sodium carbonate concentration of about 100 ppm. It suggested that the agent accelerated both the recombination and scission reaction. Therefore, the concentration at which the rates of both reactions are the same can be logically found. If the materials and self-repairing materials are found, it may be called ‘damage-free material’ which never deteriorates.

The third is the necessity of ‘selectivity’ or ‘memory’ in active protection. The function of active protection is repair. ‘Repair’ means the recovery from the deterioration state to the inherent structure. Meanwhile, the function of passive protection is not to repair but to guard materials. It is the qualitative difference between the two kinds of protection systems as mentioned in the previous section. Namely, the selectivity or the memory of the inherent structure is necessary to repair it perfectly.

The ‘selectivity’ means that the repairing agent reacts with only the damaged site. For example, when DF attacks a polymer chain and cuts it, there are two kinds of ends in the polymer. However, it is difficult for the repairing agent to discriminate between the scission end and the end of the original chain. So, when the recombination reaction cannot select the scission end and its rate is fast, the molecular weight of the repaired chain is liable to be higher than...
the original weight. The overreaction is out of the question because the higher molecular weight after the processing procedure increases the strength of the polymer. It is indeed true in general uses but it is not always suitable for industrial materials.

‘Memory’ is a more difficult problem. Even when the repairing agent has high selectivity, it cannot decide whether the present state is the same as the original state. In particular, the materials integrated in many industrial goods are used in various circumstances. Some of them will be damaged by many kinds of DFs and they will deteriorate unexpected structures. This problem remains unsolved. Perhaps a sophisticatedly programmed memory or an information system able to process unexpected damage is necessary.

Finally, the items and the necessity of further research work related to self-repairing design will be summarized.

The chemical or physical structure at the initial state and just after deterioration is crucial in designing a self-repairing system. However, the analysis of the damaged site is very difficult because the change at the beginning of deterioration is slight compared to huge atoms and crystals that compose plastics, metals, ceramics and composites. It is one of the actual obstacles in conducting successful experiments.

There have been many efforts to elucidate the deterioration reaction of plastics [51–53]. In particular, plastics for general use such as polypropylene (PP), polystyrene (PS) and polyvinylchloride (PVC) and engineering plastics such as PC, PPE, polyamide (PA), polybutylene-telephthalate (PBT) have been fully discussed in terms of deterioration by heat, light, oxygen and external mechanical force. The degradation routes of PC and PPE [54–57], whose self-repairing systems are introduced in this paper, have also been studied and published.

Although there are many papers on the degradation of PC and PPE, it cannot be directly applied to the designing of self-repairing materials for the following reason. In study on self-repairing materials, not only the degradation stage itself but also transitional period from normal (initial) stage to degradation one must be analyzed quantitatively. However, the analytical methods of this transitional period in polymers have not been established.

Recently, as one of analytical methods of this period, the ‘Molic-mouse’ method, designed to analyze initial and quantitative degradation routes, was developed [58,59]. When the calculation of the initial stage is required, the quantitative data are simulated using the degradation data at higher temperature and extrapolating them to the lower degradation region. The degradation paths and the scission products of several polymers were quantitatively simulated by the Molic-mouse method [60,61].

On the other hand, the structural damage by external mechanical force has also been researched in detail.
In particular, those of PC and PPE were investigated by dynamic viscoelastic measurement [62,63]. These fundamental results on the chemical degradation and the physical damage of polymer are very important information to investigated self-repairing plastics.

3. Protection system in a living body compared with man-made materials

Eleven kinds of systems with sophisticated and complicated protections in a living body are listed in Table 3. The protection mechanism is considerably more ingenious than that of man-made materials, as it has been indispensable in conserving the species in a very long evolution history [64].

A living body is constructed of proper materials suited for the parts of its body. Bone, nail, hair and skin are typical examples that are composed of special protein and inorganic materials.

The second protection level is the exclusion of deterioration elements such as Hg, As and eliminating dangerous living bodies. These elements become concentrated in the nail and hair and are removed outside the body. Antigen–antibody and leukocyte are important protection systems that take charge of the attack from various harmful materials and living bodies.

The third is passive and active protections. The passive protection is prepared before the attacks from DF hand in advance. They have been constructed though many experiences in a long evolution process. However, the various attacks from the surroundings are often so unexpected that a living body cannot cope with DF only by the passive protection. Therefore, it is indispensable to have systems that can deal with the unexpected situations.

For example, there are many causes of cutting out a part of a body simple injury caused by oneself or damage inflicted by an enemy or intentional removal such as surgery. Skin sclerous or tyloma is one of the passive protections against these. The missing tissue, however, can be regained by the passive protection process. The recovery is the role of active protection.

Higher order protections such as apoptosis, abolition of tissue, pause or substitute of metabolism or function have been established in a body (from No. 8 to No. 11 in Table 3).

There are some advanced protections besides the systems listed in Table 3. If a living body could know of dangers ahead of time, it could avoid them. This protection can be classified as active protection, whereas it cannot be identified as a physical or chemical structure in the living body. The ‘soft’ protection system is put into operation by the brain and it is a kind of posteriori protections.

Although the classification in Table 3 is common in almost all living bodies, each of species, phylum, or division has one's own specified protection systems. A tree is one of the typical examples of living bodies that take nutrition without any predation [65]. The cambium and the neighboring layers, which are thin and located between the skin layer and the inner part, are the only active sites in a tree. Some of the cells were born in the cambium and were pushed to the outer part. They die in the following year and change to cork. Subsequently, they become the bark, which is dead cells and whose role is the protection of a tree from severe circumstances such as wind, rain and ultraviolet rays in sunlight. The bark will be worn off in several years. Such strategy of protection for the outer part of a living body is widely seen both in autotroph and heterotroph and can be called ‘periodical abolition’ [66].

Almost all cells remaining in the inner part also die in the following year. A few percent of the cells called the ‘watch cell’ are alive and protect other cells from DF. This site is called ‘sapwood’ and the colour is white or milky-white.

As cells are synthesized every year by the cambium, the cells synthesized in the previous year move to the central part of a tree. This causes the formation of annual rings. After 10 years or more, the watch cells also move to the central part secreting colored and scented preservatives and antiseptics such as cresols and lignin. This is the preparation of the change of the protection system, and all of the watch cells die [67].

The colored part is called ‘heartwood,’ which is protected by chemicals. Generally speaking, the active

| No. | Classification | Point | Example |
|-----|----------------|-------|---------|
| 1   | Materials      | Materials selection | Nail |
| 2   | Exclusion      | Exclusion of deterioration elements | Specific proteins |
| 3   | Eliminating dangerous living bodies | Antigen–antibody reaction |
| 4   | Protection     | Passive chemical protection | Melanin |
| 5   | Passive physical protection | Gastric secretions |
| 6   | Active protection | Repair of thymine dimmer |
| 7   | Stimulation-response effect | Stomach wall’s protection against alcohol |
| 8   | Abolition      | Apoptosis | Suicide of damaged cells |
| 9   | Abolition of tissue | Tree bark, Stomach wall |
| 10  | Pause of metabolism or function | Heartwood |
| 11  | Substitute     | Substitute | Internal organs |
protection in the sapwood is superior to the passive protection in the heartwood because the former protection can meet against various unexpected attacks.

By the way, it is important for a tree to be higher than the one standing next to it. If the tree is shorter, it receives less sunlight, which means it lacks enough energy to survive. For the tree to grow taller, the trunk needs to become bigger. However, sunlight alone is not enough to give energy to all of the cells in a tree even if the tree is the tallest in the forest. This dilemma was solved through the stopping metabolism of almost all the cells composing the tree. In other words, the dead cells support the tree. Because solar energy is very thin and fluctuates, a tree has a system in which the energy consumption necessary for survival is minimized. Biological activities such as breeding, metabolism, repair and other various activities require energy. The analogy between PPE self-repairing and the active protection system in a living body like a mammal will be considered.

A man consumes carbohydrate and other foods every day and stores them in his body as glycogen and various compounds. Also, oxygen is inhaled through the cells of the lung and is carried to the cells in his body through the blood vessels by the Fe–organic complex. The oxygen reacts with the carbohydrate composed of carbon and hydrogen to emit energy, carbon dioxide and water. Although many compounds such as ATP and intermediates in the Krebs cycle participate in the serial activities, the overall reaction is the reaction of oxygen with carbon and hydrogen.

The career of oxygen or electron is the Fe-complex in mammals or the Cu-complex in PPE. The carriers and carrying routes are compared in Fig. 11.

In order to continue the repairing system in a PPE specimen, the supply of hydrogen and oxygen and the removal of water are indispensable. As about 1.2 V of electron reduction potential between proton and oxygen ion can be used. Although Cu (I) is a deactivated ion and is regenerated by oxygen, all of Cu (I) are not oxidized to Cu (II). If 90% of Cu (I) changes to oxidized state, the electron potential of the reciprocation is about 0.12 V at room temperature. So, the energy efficiency is about 10% to continuously drive the self-repairing action.

Excrement is generated though activities. Carbon dioxide and water are the excrement generated in the process of energy acquisition. These two and other compounds whose origins are various metabolic activities in a living body are emitted. Water emission from PPE or phenol accumulation in PC can be called the excrement from man-made materials.

As for polyether-ketone (PEK), two kinds of reactions participate in the protection system. One is the ester exchange reaction and the other is a recombination reaction of two polymer ends as eliminating KF. The overall reaction system is summarized in Fig. 12.

The other interesting point is ‘repairing timing’. A living body is a very sophisticated complex in which each organ acts out its function and guards against attacks without interruption. For example, the thymine dimmers on DNA, one of the most famous deterioration factors that triggers skin cancer, is generated under the skin by the several thousands per 1 h under summer sunlight. If some of thymine dimmers fail to be self-repaired, the living body will be forced to directly fight the cancer.

A similar phenomenon was observed in the PPE repairing experiments where the specimens were put in
a chamber to regulate oxygen partial pressure. When the oxygen supply was continuous, the recovery was smooth. But recovery was impossible after a long interval of no oxygen supply. This suggested that the structural change was large and inverse reaction was impossible after a certain period.

Finally, the authors would like to shortly comment on the concepts of ‘breathing’ of man-made materials and in a living body.

‘Breathing’ has been generally regarded as one of activities peculiar to living things for a long time. However, a PPE specimen appears to breathe. It inhales or breathes in oxygen and exhales or breathes out. Some phenomena, which have been tacitly understood as activities of life, may possibly not be peculiar to living things.

4. Summary

The studies on self-repairing systems of materials, especially those of plastics, are reviewed. And also, the self-repairing phenomena in man-made materials are compared with that in a living body at the molecular level. The summary is as follows:

1. Self-repairing phenomena were observed in several polymeric materials.
2. The molecular weight of PC decreased by hydrolysis was recovered with sodium carbonate catalyst as a self-repairing agent.
3. The tensile strength of PC increased after it dropped down by hydrolysis treatment.
4. The larger the deterioration of the molecular weight, the higher the recovery rate.
5. Antagonism between deterioration and repairing and the apparent molecular weight will be constant at the optimum concentration of the repairing agent.
6. Continuous repair was observed in PPE specimens, in which a repairing and an energy cycle like metabolism in a living body could be deduced.
7. Oxygen or electron transfer systems in a living body were similar to those in the PPE specimen.
8. Excrement is generated in every self-repairing system. One was carbon dioxide and water as a result of the energy cycle and another origin of the excrement was an eliminated fragment from the damaged site.

The fundamental information of the polymer chain in degradation was indispensable in designing a repairing system. In particular, a quantitative approach and structural change at the initial stage were very important.

The comparison between the repairing system of man-made materials and that in a living body is meaningful in promoting the acquisition of information on life as well as the study on self-repairing systems.

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