

Proposal for Dismantlable Adhesives to Support Circular Economies

Introduction

Adhesives are a cost-effective, lightweight and easy way to join surfaces together and can be designed to join different materials, such as joining metal to plastic. They are used in a wide range of industries. In terms of separation, dismantling, reuse and recycling, in many cases, materials and components joined with adhesives are more difficult to separate than those joined with mechanical methods such as bolts. This is one source of difficulty in the realization of circular economies, a term that has become more common in recent years. Efforts to solve this issue inspired the development of “dismantlable adhesives,” which allow for removal after curing. In this article, the authors provide background information, describe the current state of development and outline challenges to be overcome in this area.

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1. Barriers to the Realization of Circular Economies

In this section, the authors explore barriers to the realization of circular economies from the perspective of an adhesives manufacturer.

The sound of initiatives channeling the philosophy of the sustainable development goals (SDGs) and carbon neutrality into concrete action is growing louder day by day. In the adhesives industry, progress has been made in attempts to reduce the energy used to cure adhesives, namely by reducing the required curing oven temperature or shifting to products that can be cured at room temperature.¹⁾ Progress is also being made in switching to biomass-derived raw materials for adhesives.²⁾

Looking at society as a whole, scenarios are being set out in which carbon neutrality is achieved through actions such as the adoption of EVs and energy production methods that do not rely on fossil fuels, including solar and wind power.³⁾ At the same time, International Energy Agency (IEA) calculations⁴⁾ indicate that, in order to achieve the Paris Agreement targets of limiting global warming to 2°C (1.5°C) or less, production of lithium, nickel and other minerals crucial for clean energy must quadruple over the next 20 years. In addition to these circumstances, in Japan, the Japanese Ministry of Economy, Trade and Industry (METI) is aiming to establish a “growth-oriented resource-independent economic strategy” due to the country’s low level of mineral self-sufficiency and the fact that certain minerals are produced in a limited number of countries. It has set out a mission of working to enhance the independence and resilience of Japan’s domestic resource conservation systems as a route to strong growth.⁵⁾ The circular economy (CE) that METI strives for against this backdrop is shown in Figure 1. (Based on Japanese document created by METI. English

translation by ThreeBond.) The circulation marked with red arrows indicates the flow of resources through the CE, while the black arrows indicate the flow of resources in the conventional linear economy (mass production and mass consumption).

While several CE loops are depicted, it is generally preferable for circulation to take place within the inner loops. This is because the outer loops have higher costs. In other words, it is desirable that produced components be used for a long time, until the end of their lifespan.

Recycling-related regulations in Europe are another topic that has been unavoidable in recent years. The EU Circular Economy Action Plan sets out a plan for regulations to accelerate the use of recycled materials. For example, it specifies that at least 25% of plastic used to build automobiles must come from recycling.⁶⁾ In addition, at least a certain ratio of the mineral materials used in batteries must be recycled raw materials.

Based on the overall societal issues described above, it seems reasonable to say that adhesives with the following characteristics will be sought.

- 1) Longer adhesive bonding lifespans
- 2) Easier dismantling of adhesive bonds

Increasing the lifespan of adhesive bonds is something that conventional adhesives also require, and with circulation around the inner loops in Figure 1, longer product lifespans are more desirable. This means that the adhesives used to joint components should also have a long lifespan. On the other hand, easy dismantling of adhesive bonds is required when resources from products must be collected. Taking motors as an example, steel and magnets joined with adhesives are disposed of as waste if they remain adjoined. However, if they can be separated, it would be possible to reuse both as resources.

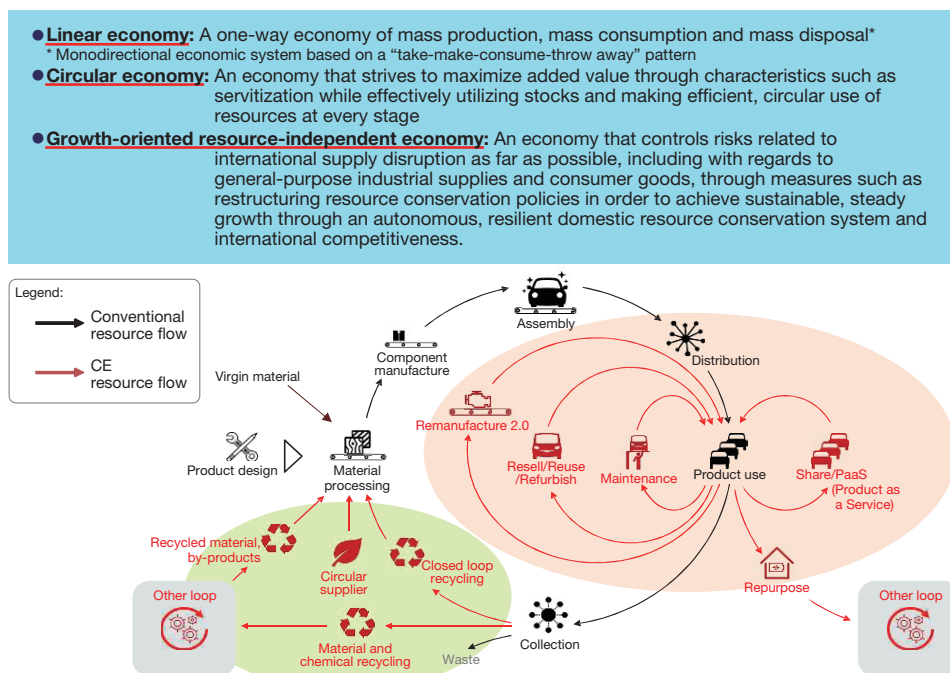


Fig. 1 Circular Economy and Growth-oriented Resource-independent Economy

Based on this, it can be said that easy disassembly of adhesive bonds is a means to achieve the resource-independent economy that METI strives for.

However, adhesive bonds with a long lifespan and easy disassembly can also be described as bonds that “stick together well and can be easily separated.” In other words, it requires that two diametrically-opposed functions be incorporated into the adhesive design. These tradeoffs are the barriers to the realization of circular economies from the perspective of an adhesives manufacturer described at the beginning of this article.

2. Overview of Dismantlable Adhesives

In order to achieve the aforementioned bonds that “stick together well and can be easily separated,” external stimulation during peeling apart is key. In this section, the authors present examples of previously-reported dismantlable adhesives with a focus on external stimulation, in other words, the “dismantling triggers” used when peeling apart adhesive bonds.

Triggers for known dismantlable adhesives include light, heat, ultrasonic waves, electricity, and contact with chemicals. It is crucial that dismantling occurs rapidly when these dismantling triggers are enacted and that dismantling triggers are not enacted unintentionally. Figure 2 shows dismantling over time for dismantlable adhesives. The black line in the same diagram shows an ideal case, in which the bond strength of a cured adhesive falls rapidly with high contrast in a short time after exposure to an external dismantling trigger. On the other hand, the red line shows an undesirable case, in which the bond strength decreases as if exposed to a dismantling trigger despite the fact that no dismantling trigger has been enacted. For example, it is undesirable to use dismantlable adhesives with light as a dismantling trigger in designs that may be exposed to light or to have heat sources near areas where a dismantlable adhesive with heat as a dismantling trigger is applied.

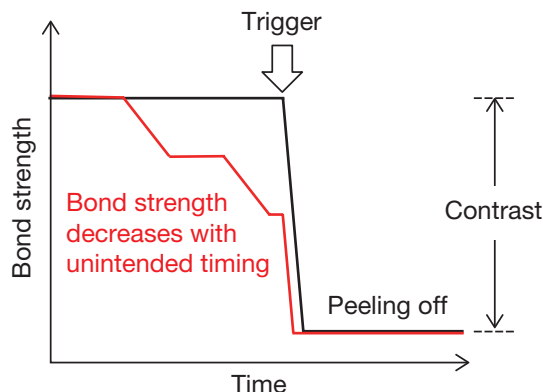


Fig. 2 Bond Strength of Dismantlable Adhesives Over Time

Alongside the aforementioned dismantling triggers, the mechanisms by which adhesives peel off are also of interest. While various types exist, the main categories are shown in Figure 3 and Table 1.

Dismantlable adhesives can be broadly separated into two types of cured adhesive: decomposing and non-decomposing.

With decomposing types, reactions occur that break the molecular bonds that make up the cured adhesive, which in turn causes the cohesion of the cured adhesive to decrease, leading to dismantling. While there are various types of decomposition reaction, the dismantling triggers generate a compound that act as a catalyst to promote the decomposition reaction within the system. If the trigger is a chemical, the chemical itself causes the decomposition reaction. If the trigger is irradiation with light, the reaction to the light can be considered the decomposition reaction. In any case, the adhesive strength decreases due to decomposition of the cured adhesive. As a result, the failure mode is cohesive failure in many cases.

There are also several mechanisms to consider with non-decomposing types, which do not undergo decomposition reactions. Examples include volume expansion (swelling)

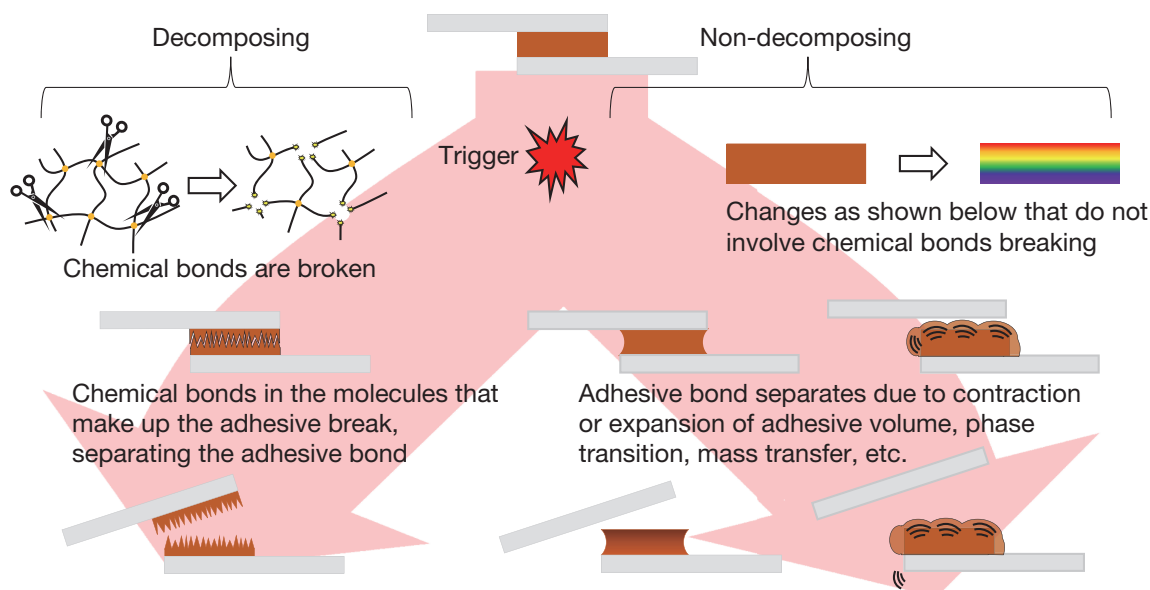


Fig. 3 Dismantling Triggers and Mechanisms of Dismantlable Adhesives

Table 1 Examples of Research on Dismantling Triggers and Mechanisms of Dismantlable Adhesives

Type	Trigger	Mechanism	Reference
Non-decomposing	Heating	Expansion of enclosed capsules	7
Non-decomposing	Chemicals	Swelling and dissolution of resin	8,9
Decomposing	Light	Photodecomposition reaction	10,11
Non-decomposing	Light	Phase transition	12,13,14,15
Decomposing	Heating	Heat \Rightarrow Catalyst generation \Rightarrow Decomposition	16,17
Decomposing	Heating	Thermal decomposition	18,19
Non-decomposing	Heating	Volume contraction, linear expansion difference	20
Decomposing	Ultrasonic waves	Ultrasonic waves \Rightarrow Catalyst generation \Rightarrow Decomposition	21
Non-decomposing	Electricity	Component segregation	22
Decomposing	Chemicals	Chemical-induced decomposition	23

and contraction, phase transition, and mass transfer of the cured adhesive.

For volume expansion (swelling), thermal expansion microcapsules can be added to the adhesive and expanded when dismantling is desired,⁷⁾ or swelling of the cured adhesive could be induced with a solvent or other substance.^{8,9)}

In the case of volume contraction, heating unreacted reactive points to high temperatures promotes a reaction, and internal stress due to volumetric contraction leads to dismantling.

Phase transitions are when the cured adhesive changes phase due to the dismantling trigger. For example, a change from a solid to a liquid can decrease the bond strength.

With mass transfer, the plasticizer component in the cured adhesive moves to the interface, decreasing the bond strength at the interface. For these non-decomposing dismantlable adhesives, the failure mode is often interfacial peeling.

Combining dismantling mechanisms and dismantling triggers in these ways enables the design of dismantlable adhesives.

In the following section, the authors present some examples of research including the aforementioned triggers and mechanisms. The first example is a dismantlable adhesive with light as the trigger. Suyama et al. have reported an example of adding a (meth)acrylate crosslinking agent with units that decompose with photoirradiation into adhesive compositions.^{10, 11)} In this example, as shown in Figure 4, the crosslinking points decompose with photoirradiation, decreasing the adhesion of the adhesive. This enables dismantling of adhesive bonds.

Beyond this photodecomposition, examples of reducing bond strength through photoirradiation-induced phase transitions have also been reported. Using the light-induced phase transitions associated with photoisomerization of azobenzene units, irradiation with light changes the adhesive component from a solid to a liquid, controlling the bond strength.¹²⁾ In a similar vein, examples of research into controlling bond strength using phase transitions of N-benzylideneaniline from a liquid crystal phase to an isotropic (liquid) phase have also been reported.¹³⁻¹⁵⁾ Methods that use these phase change-related dismantling mechanisms differ from the previously-mentioned dismantling reactions in that they are reversible. As a result, it can be said that the adhesives are reusable.

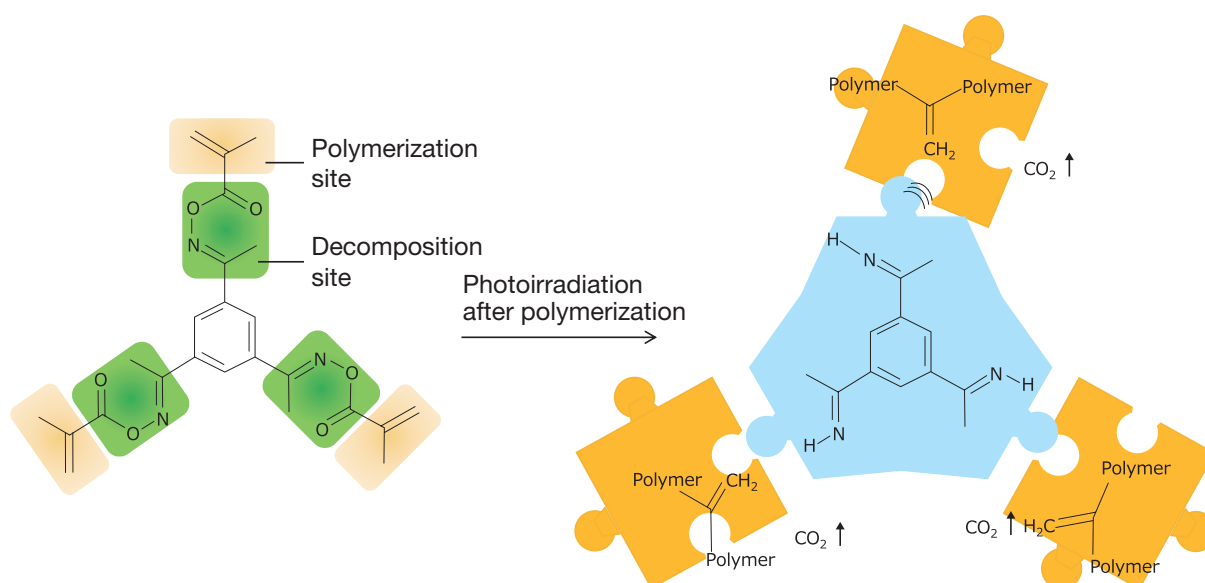


Fig. 4 Examples of Chemical Structures in which Photoirradiation-induced Chemical Bond Breaking Occur

The next example is research on a dismantlable adhesive with heat as the trigger. Sato et al. have reported adhesives with poly peroxide structures^{16, 17} as shown in Figure 5 and anthracene dimer structures.^{18, 19} When these cured adhesives are heated, in the former type, the latent reducing agent in the adhesive composition becomes apparent and the peroxide part detaches, reducing the bond strength. For the later type, heating the anthracene dimer structure causes decomposition and thermal dissociation, reducing the bond strength.

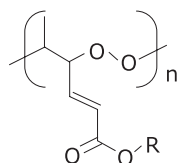


Fig. 5 Poly Peroxide Chemical Structure

Sato et al. have also reported research on non-decomposing types using heat as a trigger.²⁰ Hyperbranched polymers containing two types of curable functional groups, such as acrylic and epoxy groups, in the side chain are added to the adhesive composition, and the reactions of these functional groups are used to cure and break down the adhesive. In other words, some reactive functional groups are consumed as part of the adhesive curing reaction, enabling the formation of a stable cured material. When dismantling is desired, the cured material is heated above the curing temperature, causing the functional groups that have not yet reacted to react. When this occurs, internal stress due to additional curing shrinkage and the difference in linear expansion between the adherend and adhesive reduce the bond strength, leading to interfacial peeling. One notable feature of this method is that the adhesive composition does not decompose, rather interfacial peeling occurs.

The next example is research on a dismantlable adhesive with ultrasonic waves as the trigger. Tachi et al. have reported dismantlable adhesives in which microcapsules containing a thermal acid generator are added to an adhesive with an acetal structure.²¹ Acid causes acetal to decompose, so the capsules are broken with ultrasonic waves to release the acid generator within, breaking chemical bonds in the adhesive composition to enable the reduction of the bond strength.

There also exists technology that, while being an adhesive, can be made to peel off by applying voltage.²² Ionic liquids or other ionic components are added to these adhesives, and when a voltage is applied, ions near the electrodes segregate at the electrode interface, reducing adhesive strength. It has been reported that, because this is a phenomenon based on mass transfer, it can also be used repeatedly.

The final type is dismantlable adhesives that make use of chemicals. When these adhesives come into contact with externally-supplied chemicals, certain chemical bonds

within the adhesive composition are broken, reducing the bond strength. One example that can be pointed to is adhesives containing diacylhydrazine structures that are decomposed using oxidizing agents.²³ As shown in Figure 6, the diacylhydrazine structures decompose into carboxylic acid and nitrogen gas. If the adhesive is designed such that this structure becomes a crosslink, the bond strength can be reduced by bringing the bond section into contact with oxidizing agents.

While a comprehensive description of every research case is beyond the scope of this article, the above is sufficient to show the wide range of ideas that exist.

It can be difficult to select a dismantling trigger and mechanism from among these options. However, based on the twin considerations of longer adhesive bonding lifespans and easier disassembly of adhesive bonds, ThreeBond has chosen to work on developing dismantlable adhesives that use oxidizing agents as triggers. The main reason for selecting this method is that dismantling does not occur at unintended times. Oxidizing agents used with this method do not exist anywhere in nature, which means that they have a lower risk of shortening adhesive lifespans due to the dismantling mechanism when compared to light and heat triggers, to which unintentional exposure in nature is conceivable.

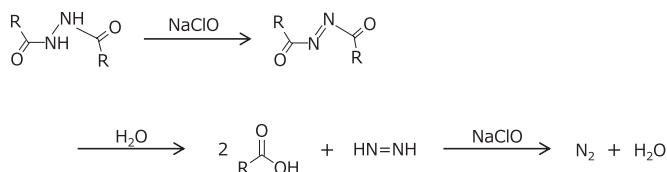


Fig. 6 Oxidative Decomposition of Diacylhydrazine Structures

3. Oxidizing Agent-induced Dismantling of Dismantlable Adhesives

In this section, the authors describe the aforementioned oxidizing agent-induced dismantling adhesives. To begin with an explanation of the oxidizing agent-induced dismantling chemical reaction, as shown in Figure 6, the diacylhydrazine structure is decomposed by oxidizing agents. The oxidants used here are compounds such as sodium hypochlorite, nitric oxide, and nitrogen dioxide. The dicyclohexazine structure is not oxidized by oxygen in air. In addition, prior to oxidation, N-N bonds are thermally stable and undergo cyclodehydration without decomposing at high temperatures exceeding 300°C and form stable aromatic rings. In summary, diacylhydrazine structures have excellent thermal stability prior to oxidative decomposition.

In this respect, diacylhydrazine structures are extremely stable before being acted on by the oxidizing agent as

a trigger. However, they decompose immediately after coming into contact with a sodium hypochlorite aqueous solution (chemicals used as kitchen bleach in homes), which are oxidizing agents. Figure 7 shows a cured adhesive into which diacylhydrazine structures have been introduced that has been immersed in a sodium hypochlorite aqueous solution. It can be seen that the strip of cured adhesive foams violently as it decomposes. In other words, diacylhydrazine structures offer chemical structures that are stable during use but can be separated rapidly when desired.

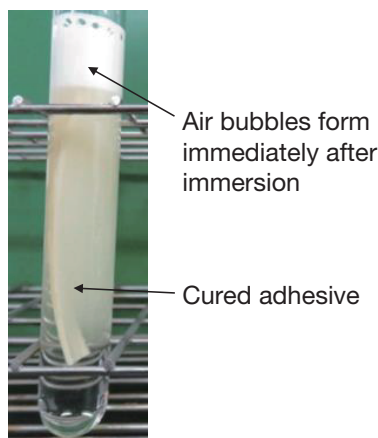


Fig. 7 Cured Adhesive with Diacylhydrazine Structures Introduced Immersed in a Sodium Hypochlorite Aqueous Solution

Oguri et al. have reported adhesive compositions synthesizing phenolic resin with diacylhydrazine structures that are cured using epoxy resin and imidazole catalysts.²⁹⁾ In this paper, it has been shown that adhesive bonds peel off when combinations of various diacylhydrazine-containing phenolic resins and epoxy resins are immersed in a sodium hypochlorite aqueous solution as described above. In addition, the 5% weight loss temperature (pyrolysis temperature) of cured products of phenolic resin and epoxy resin synthesized is high in all of these cases, approximately 300°C. From these reports, it can also be said that adhesive compositions with diacylhydrazine structures are highly likely to be able to realize both aspects mentioned at the beginning of this article: the long lifespan and easy dismantling.

As a result, ThreeBond is exploring adhesive compositions that have diacylhydrazine structures. While several approaches are being implemented in parallel, in this article the authors will discuss the efforts that are closest to practical application.

The research discussed thus far involves synthesizing new compounds and using them as raw materials for adhesives. Regulations concerning chemical substances in products differ by country, which means that new compounds must go through registration and toxicity

evaluation in various countries in order to be widely used worldwide. This slows down practical application. Given this background, ThreeBond decided to avoid using new chemical substances in consideration of achieving early industrial use and set out to try and create the aforementioned diacylhydrazine structures by combining previously-registered chemical substances. The authors describe the content of this study in the next section.

4. Trial Product Under Development

Examination of materials for use in the creation of dismantlable adhesives that decompose with oxidizing agents led to dihydrazide compounds, which have a track record in substances such as epoxy resin curing agents. Hydrazide's chemical structure is shown in Figure 8. There are NH₂ structures at the ends which enable curing through reactions with epoxy resin. This chemical structure is similar to the aforementioned diacylhydrazine structures, so it seemed possible that the same functions could be brought out. Hydrazide compound chemical reactions are summarized in Figure 8. It shows reactions with acrylic groups, epoxy groups, isocyanate groups, and halogenated compounds such as alkyl halides and acid chlorides as examples. Acylhydrazine structures are formed in all of these reactions. It has been confirmed that monoacylhydrazine can also be decomposed by oxidizing agents, and it was determined that these chemical reactions could be expanded to dismantlable adhesives.

At present, trial products using reaction (1) from Figure 8 are being examined, and sample work has started on adhesives using two-component type acrylic resin as the main component. A composition in which one side contains a dihydrazide compound and the other side contains a compound with acrylic groups is used, and the chemical reaction shown in (1) cures the adhesive. The properties and physical characteristics of the trial product are shown in Table 2.

The initial tensile shear bond strength is over 10 MPa, achieving bond strength suitable for use on a wide range of components. In addition, as described earlier, acylhydrazine structures have high thermal resistance, and it has been confirmed that their strength does not decrease, even after high temperature durability testing (Table 2).

In terms of removability, tensile shear bond strength has been confirmed, and peeling of the test piece after immersion in a sodium hypochlorite aqueous solution at room temperature has been confirmed.

In this respect, the trial product can be considered close to practical application in terms of both heat resistance and removability. However, it is possible that immersion in sodium hypochlorite aqueous solutions would increase the burden of actual recycling processes.

Table 2 Physical Characteristics of Trial Product

Test item	Unit	Measured value	Testing method	Remark(s)	
Hardness	—	A84	3TS-2B00-010	—	
Tensile shear bond strength	Blank	MPa	13.7	3TS-4100-023	SPCC-SD
	Blank	MPa	10.8		A1 (A1050P)
	NaClO aq. after immersion	MPa	2.5		SPCC-SD
	After immersion in 60°C engine oil	MPa	12.3		
	After immersion in 150°C engine oil	MPa	16.3		
	150°C, 720 h	MPa	25.6		
	180°C, 720 h	MPa	19.8		
T type peeling adhesive strength	kN/m	1.7	3TS-4130-021		

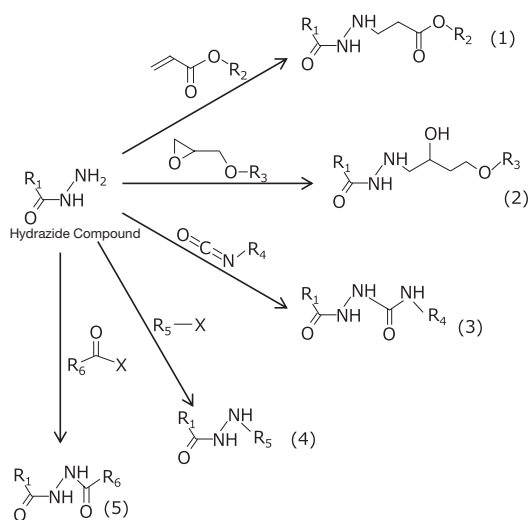


Fig. 8 Examples of Hydrazide Compound Chemical Reactions

For this reason, adhesive dismantling using dry processes is also being examined. The adhesive bond product was placed in an airtight container, into which nitric oxide and nitrogen dioxide gases were inserted as oxidizing agents to promote decomposition of the acylhydrazine structures. The results of shear bond strength testing at that time are shown in Figure 9. With both nitric oxide and nitrogen dioxide, reaction progressed in a similar manner as with sodium hypochlorite, and it has been confirmed that bond strength is reduced. This process uses a gaseous oxidizing agent, which means that processing can be completed simply by treating the gas in an airtight container. Unlike immersion in an aqueous solution, this can be said to reduce the post-processing burden.

Formations have also been proposed whereby conventional non-decomposing adhesives are used for the adhesive, and a thin layer of dismantlable adhesive similar to the trial product is applied in advance to provide dismantlability in the adhesive bond.²⁴⁾ (Figure 10) This method would enable dismantling of components while using conventional adhesives.

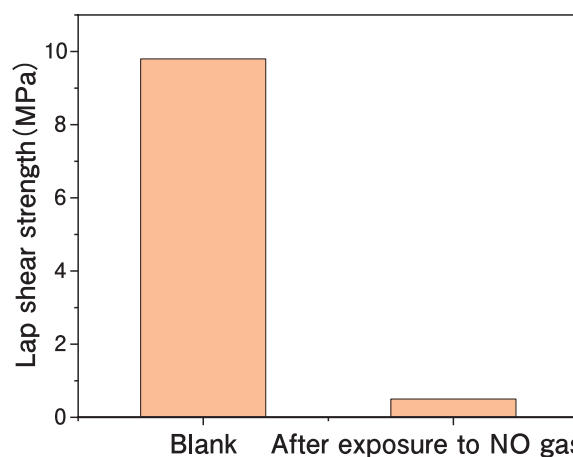


Fig. 9 Changes in Tensile Shear Bond Strength with Use of Nitric Oxide and Nitrogen Dioxide on Decomposing Adhesive

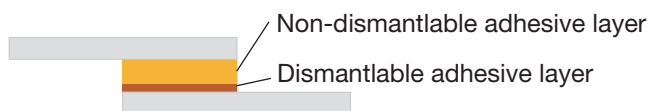


Fig. 10 Method for Adding Dismantlability to Adhesive Bonds when Using Non-decomposing Adhesive

While oxidation-induced dismantling is a single concept, ThreeBond is preparing proposals for several processes based on this idea. However, the complex process of separating adhesive bonds is no easy task. Lower-cost recycling cannot be achieved through the efforts of adhesive manufacturers such as ThreeBond alone. Understanding the characteristics of adhesives from the component design stage is crucial, and there must be effective cooperation between component designers and adhesive manufacturers such as ThreeBond as further examination moves forward.

Even among adhesive manufacturers, ThreeBond has always produced wide-ranging products in small quantities and has been notable for developing products that align with customers' needs. Leveraging these strengths, it will continue working to realize circular economies, which can be considered a social need, through the development of adhesives.

Closing

In this Technical News article, the authors described efforts relating to dismantlable adhesives. Dismantlable adhesive technology can be said to be in its early stages, and it is not yet clear which methods will become popularized. ThreeBond is also considering various adhesive bond dismantling methods beyond those mentioned in this article. In these studies, matching component and adhesive designs is the most important consideration, and communication between adhesive users and manufacturers is crucial. With this in mind, ThreeBond will continue to develop products that support circular economies and hopes to contribute what it can to the development of this field.

Finally, in order to build a circular economy society, it is also believed that considering behavioral changes from the perspective of general consumers is important. ThreeBond will also continue working to build a new tomorrow from this perspective.

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