ThreeBond TECHNICAL NEWS

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Biomass-based Products

Introduction

As issues relating to global warming continue to take hold across the world, reducing CO_2 emissions has become a major concern due to the significant contribution such emissions make to the greenhouse effect. In particular, industrial waste disposal relating to plastic products has grown in significance with every passing year. Biomass-derived materials have a lower environmental impact than plastic during processes such as disposal, making them worthy of discussion when considering carbon neutrality in the face of this situation. While CO_2 may be generated when biomass-derived materials are incinerated, the carbon atoms in question were already contained in CO_2 that was then converted through photosynthesis. Consequently, the effect on atmospheric CO_2 levels can be considered neutral.[1)] From this perspective, products made from biomass-derived materials can be considered to be environmentally friendly.

Against this backdrop, ThreeBond has developed and launched various products made using biomass-derived materials. In this article, the authors describe a selection of ThreeBond's environmentally-friendly biomass-based products.

Hereafter, ThreeBond is abbreviated as TB.

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1. Biomass-based Products

The main components of adhesives and sealants generally include resin components, filler components and additives. TB is developing biomass-based products by using biomass-derived materials for these components.

The Japan Organics Recycling Association (JORA) uses the following definitions in relation to biomass-based products.[2)]

(1) Products that contain biomass (renewable, organic, non-fossil material from living organisms, including shells and other inorganic materials directly produced by living organisms)

(2) Products with a biomass content of at least 10%

Based on these definitions, biomass-based products can be developed by replacing part of existing product formulations with biomass materials. However, TB has gone beyond simply developing biomass products. It is carrying out product development with the aim of increasing use of biomass-derived materials as much as possible, and making use of the characteristics of these materials to surpass the performance of existing products.

Prominent examples of products that have been created include TB1539 series elastic adhesives, TB2209 single-component low temperature curing epoxy resin and TB3049 UV-curing resin. In the subsequent sections, the authors describe the biomass materials used in each product, their biomass content, and their performance characteristics.

2. TB1539 Series Elastic Adhesives

The TB1539 series comprises single-component, low temperature curing, fast curing elastic adhesives that feature plant-derived material as a main component. The biomass material used in this series is a castor oil modified polymer, produced by chemically denaturing oil squeezed from castor beans.

Table 1 Biomass Content of TB1539 Series Products

Product	TB1539	TB1539B	TB1539K
Biomass content (%)	40	40	35

Using this castor oil modified polymer as a main component has enabled a biomass content of at least 35% to be achieved (Table 1).

The TB1539 series lineup includes TB1539 and TB1539B, which differ in terms of appearance, and TB1539K, which has been developed for improved adhesion on polycarbonate (PC). In addition to having high biomass content, TB1539 series products are REACH compliant and do not use halogen compounds or organic tin compounds, compounds which have a significant environmental impact.

2-1 Castor Oil

Castor oil is a type of natural oil obtained by squeezing and refining castor beans.3) Castor beans are grown in various regions, and countries with particularly significant production include India, China and Brazil. In terms of carbon neutrality, plant-derived biomass materials can be expected to have a greenhouse effect-mitigating impact through CO_2 absorption. Ricinoleic acid is the main component of castor oil, meaning it also boasts properties such as flexibility, low temperature performance, chemical stability and electrical properties that enable the addition of various functions when it is used as a main component in adhesives.

2-2. Curing Conditions

The TB1539 series of single-component elastic adhesives can be cured by heating for a short time (as little as 1 minute) at the relatively low temperature of approximately 60°C, overcoming the long curing times that are a disadvantage of other single-component elastic adhesives. Such characteristics can reduce energy required for heating, lower costs, and result in shorter takt times. In order to achieve curing at this low temperature, the formulation contains a thermally latent curing agent that activates at approximately 60°C.

An example of this curing behavior is shown in Figure 1, which shows changes in viscosity measurements with a rheometer when TB1539 is heated at a rate of 5°C/min.

As the temperature approaches approximately 60°C, which is the initial reaction temperature, the viscosity rises sharply before the behavior stabilizes a short time (about 1 minute) later. Figure 1 is an example of curing behavior. The curing time may vary depending on the heat capacity of the adherend.

2-3. Properties and Characteristics

The properties and basic performance characteristics of the TB1539 series of environmentally-friendly elastic adhesives are shown in Table 2.

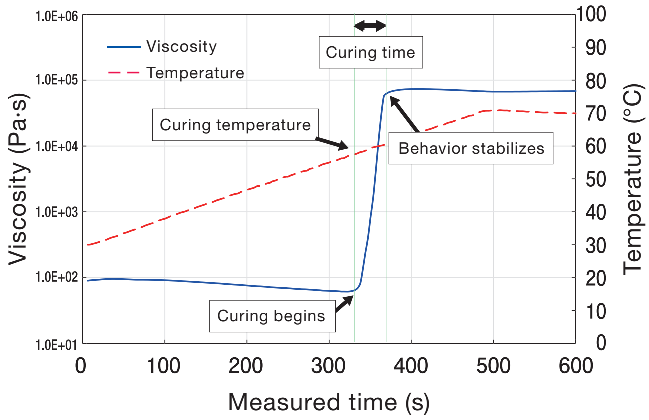

Fig. 1 Changes in Viscosity when Heating TB1539

Table 2 Properties and Basic Performance Characteristic of TB1539 Series Products

Test item	Unit	Testing Method	TB1539	TB1539B	TB1539K	Remark(s)
Appearance	–	3TS-2100-002	Black	White	Black	Visual
Viscosity	Pa·s	3TS-2F00-007	100	100	160	25°C Shear velocity 5 s^{-1}
Specific gravity	–	3TS-2500-002	1.34	1.34	1.39	25°C
Hardness	–	3TS-2B00-004	A70	A70	A74	⋆
Tensile strength	MPa	3TS-4190-001	3.5	3.5	4.8	⋆
Elongation rate	%	3TS-4190-001	120	140	230	⋆
Cure shrinkage	%	3TS-2600-001	0.02	0.02	0.02	⋆
Volume resistivity	Ω·m	3TS-5200-001	2.4×10^{11}	6.5×10^{10}	2.3×10^{13}	⋆
Surface resistivity	Ω	3TS-5200-002	7.8×10^{14}	1.9×10^{14}	5.1×10^{14}	⋆
Permittivity 1kHz	–	3TS-5220-001	6.1	5.8	5.5	⋆
Permittivity 1MHz	–	3TS-5220-001	4.9	5.0	4.4	⋆
Dielectric loss tangent 1kHz	–	3TS-5220-001	0.035	0.034	0.036	⋆
Dielectric loss tangent 1MHz	–	3TS-5220-001	0.057	0.055	0.062	⋆
Dielectric breakdown strength	kV/mm	3TS-5230-002	19	22	19	⋆
Tensile shear bond strength	MPa	3TS-4100-013	4.3 (CF)	4.1(CF)	4.0 (CF)	⋆ Aluminum
Tensile shear bond strength	MPa	3TS-4100-013	1.5 (AF)	1.4 (AF)	2.3 (CF)	⋆ PC

⋆Curing conditions: (60°C × 1.5 h) + (23°C, 50%RH) × 3 days
AF: Adhesive fracture, CF: Cohesion failure

3. TB2209 Single-component Low Temperature Curing Epoxy Resin

TB2209 is a single-component epoxy resin containing scallop shell in its formulation and can be cured at low temperatures. With scallop shell as the biomass-derived material, it achieves a biomass content of at least 40%. It provides the same or greater adhesive strength compared to TB2202, TB's standard low temperature curing type epoxy resin, while also providing environmental benefits.

3-1. Scallop Shells

Scallops mainly feed on marine plants, which absorb atmospheric CO_2 through photosynthesis. As a result, as scallops grow based on this marine plant-based diet, this carbon is transferred from the plants to the scallops and stored.

* Atmospheric carbon (CO_2) that is absorbed and stored in marine ecosystems is known as blue carbon. This is mainly produced through photosynthesis by organisms such as seaweed, seagrass and phytoplankton.[4)]

While CO_2 is released when the shells are incinerated, this can be considered the same atmospheric CO_2 that was absorbed during each shell's development. As such, there are no new CO_2 emissions from a carbon neutrality perspective.

3-2. Curing Conditions

Figure 2 shows the relationship between curing time and tensile shear bond strength for TB2209 at different temperatures.

Curing can be performed at a low temperature of 80°C × 60 minutes and high temperatures of 100°C × 30 minutes or 120°C × 10 minutes. Even with adherends that are sensitive to heating, curing can be performed in a short time at 80°C.

3-3. Properties and Characteristics

Tensile shear bond strengths for various adherend materials are shown in Table 3. Properties and basic performance characteristics are shown in Table 4.

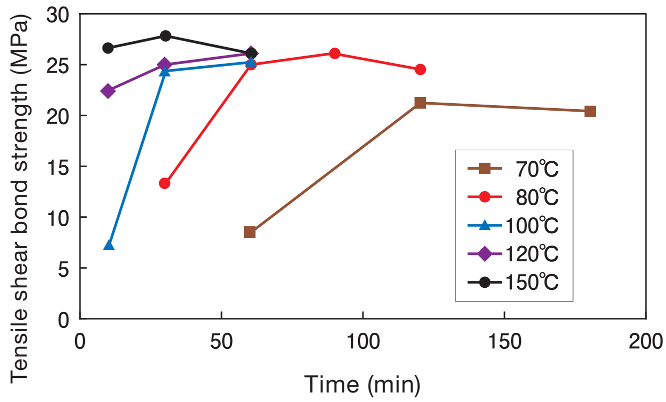

Fig. 2 Relationship between Curing Time and Tensile Shear Bond Strength by Temperature for TB2209

Table 3 Adhesion of TB2209 and TB2202 by Adherend Material

Adherend material	Tensile shear bond strength	
	TB2209	TB2202
Iron	25.0	13.0
SUS304	23.3	12.6
SUS430	23.8	11.9
Aluminum	14.3	7.8
Nickel	23.4	10.8
PBT	3.4	3.7
LCP	8.6 (*)	5.0
PC	1.8	1.1
PPS	3.5	3.3
ABS	5.7	7.3
Epoxy glass	10.3	22.6
Acrylic	3.7 (*)	1.0
Nylon 6	1.7	1.2
Nylon 6,6	2.7	1.3

Curing conditions: 80°C × 60 min (TB2209), 70°C × 50 min (TB2202)
Testing method: 3TS-4100-011
* Material failure

Table 4 Properties and Basic Performance Characteristics of TB2209 and TB2202

Test item		Unit	Testing Method	TB2209	TB2202	Remark(s)
Appearance		–	3TS-2100-002	Black	Black	Visual
Viscosity		Pa·s	3TS-2F00-007	17.4	13.0	25°C Shear velocity 5 s^{-1}
Specific gravity		–	3TS-2500-002	1.44	1.14	25°C
Hardness		–	3TS-2B00-004	D88	D88	*
Cure shrinkage		%	3TS-2600-001	2.3	2.5	*
Volume resistivity		Ω·m	3TS-5200-001	2.2×10^{13}	1.3×10^{15}	*
Surface resistivity		Ω	3TS-5200-002	3.5×10^{15}	1.5×10^{17}	*
Permittivity	1kHz	–	3TS-5220-001	4.8	–	*
	1MHz	–		4.5	3.7	*
Dielectric loss tangent	1kHz	–		0.008	–	*
	1MHz	–		0.016	0.017	*
Dielectric breakdown strength		kV/mm	3TS-5230-001	24	23	*
Tensile shear bond strength		MPa	3TS-4100-011	25.0	13.0	*, Iron
T type peeling adhesive strength		MPa	3TS-4130-021	1.8	0.2	*, Iron

*Curing conditions: 80°C × 60 min (TB2209), 70°C × 50 min (TB2202)

4. TB3049 UV-curing Resin

TB3049 is a UV-curing resin that uses plant-derived raw materials as its main component. The biomass materials are derived from pine resin and soy beans, and the product has a biomass content of at least 45%.

4-1. Pine Resin and Soy Beans

Pine resin is natural resin discharged by plants in the genus Pinus of the family Pinaceae. It mainly comprises turpentine and rosin.

Soybean oil is extracted from soybean seeds and is one of the most well-known plant oils.

UV curable acrylic acid is added to compounds refined from these materials to create the base materials for the product.

4-2. Curing Conditions

TB3049 can be cured using UV-LEDs. UV-curable resins can be broadly divided into those cured with high-pressure mercury vapor lamps and those cured with UV-LEDs. TB's UV-curable resins are generally designed to be cured with high-pressure mercury vapor lamps. However, some products can be cured with UV-LEDs. Against this backdrop, demand for UV-LED curing has grown in recent years in consideration of energy saving and reducing running costs, and TB3049 is an environmentally-friendly product in terms of its design. Curing with UV-LEDs enables power consumption to be reduced compared to high-pressure mercury vapor lamps, meaning that customer-side processes also become more environmentally friendly.

Table 5 Properties and Basic Performance Characteristics of TB3049 and TB3042B

Test item		Unit	Testing Method	TB3049	TB3042B	Remark(s)
Appearance		–	3TS-2100-002	Light yellow	Colorless, transparent	Visual
Viscosity		Pa·s	3TS-2F00-007	500	500	25°C Shear velocity 192 s^{-1}
Specific gravity		–	3TS-2500-002	1.02	1.10	25°C
Hardness		–	3TS-2B00-004	D78	D80	*1
Thick film curing performance		mm	3TS-3160-001	3.3	12.5	*2
		mm	3TS-3160-001	2.2	N/A	*3
Tensile strength		MPa	3TS-4190-001	32	72	*1
Elongation rate		%	3TS-4190-001	4.3	4.9	*1
Cure shrinkage		%	3TS-2600-001	7.0	8.4	ø32, 1.5 g, *2
Volume resistivity		Ω·m	3TS-5200-001	2.0×10^{13}	9.9×10^{12}	*2
Surface resistivity		Ω	3TS-5200-002	1.6×10^{15}	2.9×10^{15}	*2
Permittivity	1kHz	–	3TS-5220-001	3.4	4.7	*2
	1MHz	–	3TS-5220-001	3.3	4.7	*2
Dielectric loss tangent	1kHz	–	3TS-5220-001	0.008	0.008	*2
	1MHz	–	3TS-5220-001	0.011	0.031	*2
Dielectric breakdown strength		kV/mm	3TS-5230-002	31	33	*2
Tensile shear bond strength		MPa	3TS-4100-013	7.9	7.4	*2, Glass
		MPa	3TS-4100-013	8.0	N/A	*3, Glass

*1 Curing conditions High-pressure mercury vapor lamp (30 kJ/m^2) × 2
*2 Curing conditions: High-pressure mercury vapor lamp (30 kJ/m^2)
*3 Curing conditions: UV-LED (365 nm), 500 mW/cm^2 × 6 sec

4-3. Properties and Characteristics

The properties and physical characteristics of TB3049 are shown in Table 5. Data for TB's general-purpose UV-curing resin TB3042B is also shown as a comparison. TB3049 was developed with the aim of replicating the properties and physical characteristics of TB3042B. This makes TB3049 a versatile resin. In addition, while TB3042B does not support UV-LED curing, TB3049 can be cured to at least 2 mm with UV-LEDs.

4-4. Adhesive Strength of TB3049

The adhesive strength of TB3049 on various adherend materials when cured with a high-pressure mercury vapor lamps and UV-LEDs is shown in Figures 3 and 4. The adhesive strength of TB3042B when cured with a high-pressure mercury vapor lamp is also shown for comparison. Both TB3049 and TB3042B demonstrate good adhesive strength on various materials. TB3049 also exhibits higher adhesive strength than TB3042B for some materials. Even when TB3049 is cured with UV-LEDs, it demonstrates similar adhesive strength to curing with high-pressure mercury vapor lamps.

It can be used for wide-ranging applications in various locations.

4-5. Expected Effects in Terms of Reduction of Environmental Load

One of the effects that can be expected when using TB3049 is a reduction in CO_2 emissions. Focusing on CO_2 emissions during incineration, substantive CO_2 emissions for products made using biomass materials are lower than for those made exclusively from petroleum-derived raw materials (Figure 5). TB3049 has a biomass content of 45%, meaning it is 45% naturally-derived material. Based on the aforementioned approach, a reduction of approximately 45% can therefore be expected.[5)] This product can also be cured with UV-LEDs. Calculations showed that CO_2 emissions from the power consumption during UV-LED curing were about 1/10 those produced when using high-pressure mercury vapor lamps (Figure 6). As a result, a reduction in environmental impact can be expected.[6)]

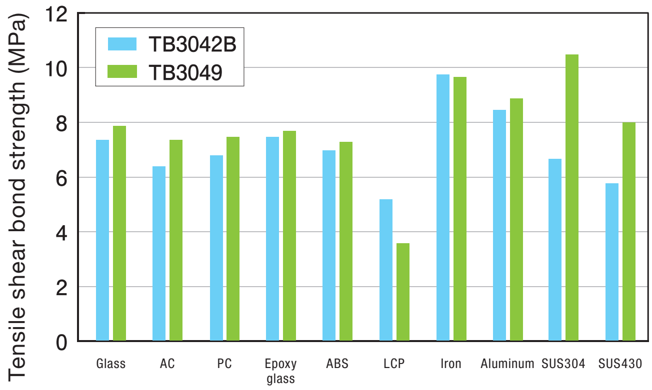

Fig. 3 Adhesive Strength of TB3049 and TB3042B by Adherend Material (Curing with High-pressure Mercury Vapor Lamp)

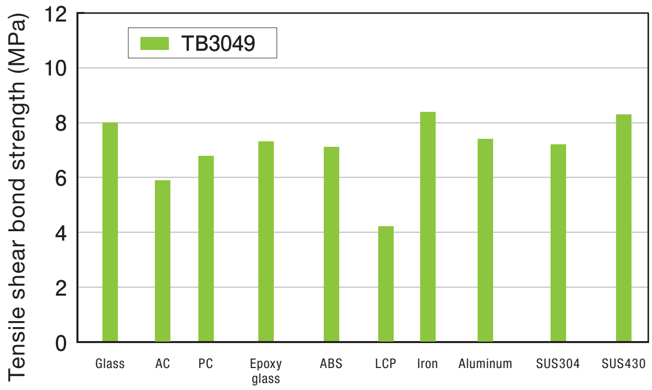

Fig. 4 Adhesive Strength of TB3049 by Adherend Material (UV-LED Curing)

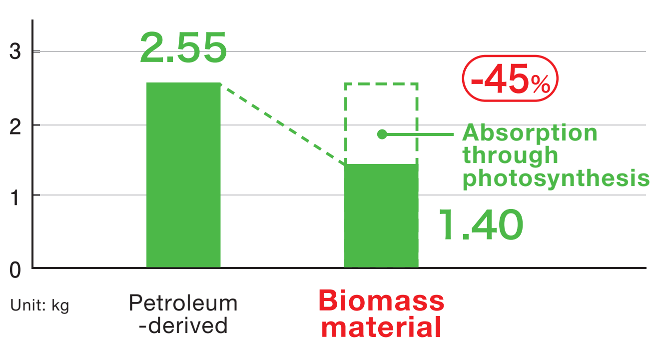

Fig. 5 Substantive CO_2 Emissions when Incinerating 1 kg of TB3049 and Product Made Exclusively with Petroleum-derived Plastics

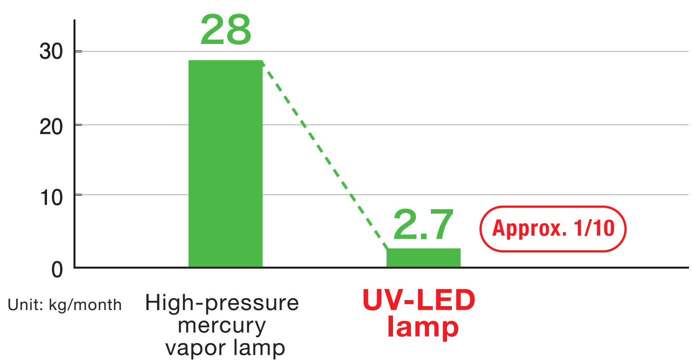

Fig. 6 CO_2 Emissions from Using High-pressure Mercury Vapor Lamps (250 W) and UV-LED Lamps (24 W) for 8 Hours per Day

Closing

In this article, the authors described TB's work on biomass-based products. TB is also reviewing the biomass content of materials used in its existing products to evaluate their environmental impact and is examining the use of biomass in manufacturing containers for products.

TB aims to contribute to technological innovation in global industry and environmental conservation by focusing on product and technology development in line with market trends. It will also continue to ensure that it provides safety and peace of mind to all stakeholders through its business activities.

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