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Structural and Engineering Adhesives

Introduction

The structural adhesive [1) 2)] is defined (JIS K6800) as a highly reliable adhesive which has less deterioration in the bonding properties even with long-term excessive loads.

Structural adhesives were fully applied for automobile brake linings which started to be used around 1960 for industrial use in Japan. In those days, brake shoes and linings had been joined using rivets, but now all brake linings for automobiles are bonded with adhesives. Structural adhesives were studied to be applied for aircrafts in 1930s outside of Japan. Many countries including Britain and the United States actually used structure adhesives for aircrafts in World War II. Today, structural adhesives are fully applied for automobile, rolling stock, electronics, building, engineering, and space industries, and they are considered to develop new applications as the leading edge adhesives for composite materials.

Engineering adhesives are also categorized as structural adhesives. Engineering adhesives are specialty adhesives, which are curing at room-temperature, nonsolvent, and liquid-reactive adhesives and provide high performance structure strength. They include six types of adhesives: epoxy, modified acrylic, anaerobic, cyanoacrylate, urethane, and silicone. This issue introduces the types, characteristics, and applications of these structural adhesives and newly developed room-temperature curing engineering adhesives.

Contents

1. Characteristics of structural adhesives

Structural adhesives have the following advantages when used in place of weldings, rivets, and bolts.

(1) Bonding between different materials

We cannot weld different materials; however, by using adhesives we can join metals with glasses and FRPs.

(2) Uniform dispersion of stress

Rivets or bolts centralizes stress on a joint part. However, glued connection can disperse stress uniformly by joining surfaces, decrease material fatigue caused by oscillations, and increase fatigue strength. Also, this reduces oscillations and prevents noises.

(3) Sealant effects

Continuous films are formed to seal joint parts.

(4) Smooth surfaces and good appearances

The adhesives do not make bumps that rivets and bolts cause or weld overlays. Without rivets and bolts, bonded objects can be lighter and smaller.

(5) Electrical insulation

The adhesives provide good electrical insulation layers to prevent electrolytic corrosion caused by contacts with different kinds of metals.

(6) Bonding durability

The adhesives provide excellent durability including adhesion performances, heat resistances, and chemical resistances.

2. Types of structural adhesives

Structural adhesives require resistances for heat, water, and chemicals as well as adhesion performances such as shearing, peeling, bending, and creep resistance. Therefore, composite adhesives containing thermal-curing resin with thermoplastic resin or synthetic rubber take a major role to provide powerful adhesive strength by heat curing. Testing standards for structural adhesives have not been established in Japan. Table 1 shows the U.S. federal standards MMM-A-132A (adhesive testing standards for aircraft structure). Table 2[1)] shows the types and curing conditions of composite adhesives corresponding to the segments in Table 1. Typical composite adhesives include vinyl-phenolic, nitrile-phenolic, epoxy-phenolic, nylon-epoxy, and nitrile-epoxy, etc. As a curing condition, they are bonded by heat and pressure at 180 to 200°C. These adhesives are used for automobile parts such as disk pads and clutch facings in addition to aircrafts.

Table 1. Requirements for structural adhesives for aircrafts

(MMM-A-132A)

Testing Item	Testing Condition		Type I Class 1	Type I Class 2	Type I Class 3	Type II	Type III	Type IV
Peeling and shearing strength (kgf/cm^2)	24°C		387	246	211	193	193	193
	82°C	10min	193	141	141			
	149°C	10min				158	141	141
	149°C	192h				158	141	141
	260°C	10min					130	130
	260°C	192h						70
	–55°C	10min	387	246	211	193	193	193
	49°C, 95 to 100 % RH 30 after days,		316	228	193	193	193	176
	24 °C, immersion in liquid after 7 days		316	228	193	193	176	176
T-type peeling strength	24°C (kgf/25mm)		23	9				
Blister detection	24°C (kgf/cm^2)		316	228				
Fatigue strength	24°C		10^6 cycles at 53kgf/cm^2					
Creep breakdown	24°C 112kfg/cm^2		Maximum deformation 0.381 mm for 192 h					
	Type I –82°C 112kfg/cm^2		Maximum deformation 0.381 mm for 192 h					
	Type II, III–149°C 56kfg/cm^2					Maximum deformation 0.381 mm for 192 h		
	Type IV –260°C 56kfg/cm^2							Maximum deformation 0.381 mm for 192 h

Note: ADHESIVE, HEAT RESISTANT, AIRFRAME STRUCTURAL, METAL TO METAL (1982-11-22)

Table 2. Types and curing conditions of structural adhesives for aircrafts

Performance		Adhesive type	Curing condition		
Type	Class	(Line)	°C	h	kgf/cm^2
I	1	Nylon-epoxy	180	1	2
	2	Modified nitrile-epoxy	120	1	0.5 to 3.0
	3	Vinyl-phenolic	180	2	14
II		Nitrile-phenolic	180	1	3
III		Nitrile-phenolic			
IV		Epoxy-phenolic	180	0.5	3
		Epoxy-phenolic			
		Polyimide	260 to 370	1.5	3 to 14

3. Performances of heating-curing one-part epoxy adhesives

The development of adhesives for general industries focuses on improving bonding strength and heat resistance and on lowering curing temperature. In place of composite adhesives described above, epoxy adhesives have become the leading adhesives.

In addition to Epi-Bis type, epoxy resins include various types such as polyether diglycidyl ether, dimer acid diglycidyl ester, urethane modified, and nitrile modified. These epoxy resins contain more than two epoxy groups in the molecule, and are used in combination with room-temperature curable curing agents such as polyamine and polyamide as well as heat curable curing agents such as boron trifluoride amine complex compound, dicyandiamide, organic acid anhydride, dibasic acid dihydrazide, imidazole, and diaminophenylsulfone. One-part epoxy is mainly used for heat-curing available components and parts.

Epoxy resins are applied for automobiles and rolling stocks because they are excellent in shearing bonding strength, creep bonding strength, heat resistance, and chemical resistance. Also they are used for electrical and electronic related products due to the excellent electrical characteristics. As an example, small motors use epoxy adhesives, which are one-hour curing at 120°C, to bond between ferrite magnets and plating steel sheets. Unlike two-part adhesives, one-part adhesives do not require measuring and compounding and have no potting life (usable life) restrictions, so we can obtain stable high quality. Table 3 shows the performances of heat-curing one-part epoxy adhesives (ThreeBond 2247).

As mentioned above, polymer alloy composite adhesives or denatured epoxy adhesives of heat-curing type have prevailed in structural adhesives. However, room-temperature curing adhesives are mainly used for materials that do not desire heating. Structural adhesives which are room-temperature curing by chemical reaction, are broadly defined as engineering adhesives.

Table 3. One-part heat-curing epoxy structural adhesives (ThreeBond 2247)

Test Item	Test Condition	Test Result
Peeling and shearing bonding strength MPa $\{kgf/cm^2\}$	25°C	29.4 {300}
	100°C	26.5 {270}
	120°C	10.8 {110}
	150°C	5.9 { 60}
	200°C	0.5 { 5}
T-type peeling bonding strength kN/m {kgf/25mm}	25°C	5.5 {14}

Curing condition: 120°C×30 minutes between soft steel sheets

4. Types and performances of engineering adhesives

Table 4 relatively compares the types and performances of structural adhesives and engineering adhesives. Both adhesives include epoxy, modified acrylic, anaerobic, cyanoacrylate, urethane, and silicone. These are nonsolvent, liquid (except for epoxy films), and reactive adhesives. Also, they are room-temperature curing and fast curing (except for one-part epoxy and films). The types and performances of engineering adhesives are shown as follows.

Table 4. Relative properties of structural adhesives and engineering adhesives

Property	Epoxy			Acrylic	Anaerobic	Cyanoacrylate	Urethane	Silicone
	Two-part	One-part	Film					
One-part	–	4	4	–	5	5	–	5
Room-temperature fast curing	2–4	1–3	1–3	5	4	5	2–4	3
Heat fast curing	4	2–4	2–4	–	–	–	2–4	–
Work lifetime	2–3	4	4	2	1	1	2–4	3
Gap filling	5	5	5	2	1	1	4	5
Surface treating requirement	2–4	2–4	2–4	4	4	2	2–3	3
Bonding strength	3–4	3–5	3–5	4	2	2–3	2–3	1
Peeling strength	1–4	1–4	1–4	3	2	1	4	4
Heat resistance	2–4	3–5	3–5	3	2	1–2	1–3	4
Water resistance	3–4	3–5	3–5	4	1	1–2	2	1
Large surface area bonding	3	3	5	1–2	0	0	3	0
Versatility	5	5	5	3	2	2	4	1

Rating: 5=exceptional, 4=very good, 3=good, 2=fair, 1=poor, 0=very poor
Source: C, L, Mahoney; Adhesive Age 29(6)13-18 1986

4-1. Epoxy adhesives

(1) Room-temperature curing epoxy structural adhesives (ThreeBond 2087)

Room-temperature curing epoxy adhesives are generally two-part adhesives that a base agent and a curing agent are mixed at a given ratio immediately before using to coat and bond. Generally-used base agents are bisphenol A diglycidyl ether resins. The curing speeds and adhesion performances may change according to combined curing agents.

ThreeBond 2087 is two-part room-temperature curing epoxy structural adhesives. By using modified polyamide as curing agents, cured objects can provide strength against peeling and impacts. They offer T-type peeling strength of 2kN/m{5kgf/25mm}, more than five times greater than existing T-type peeling strength of under 0.4kN/m{1kgf/25mm}. Room-temperature curing types are as effective as heat curing types. Figure 1 and Table 5 show the temperature dependencies of bonding strength and the adhesion performances of different materials for ThreeBond 2087.

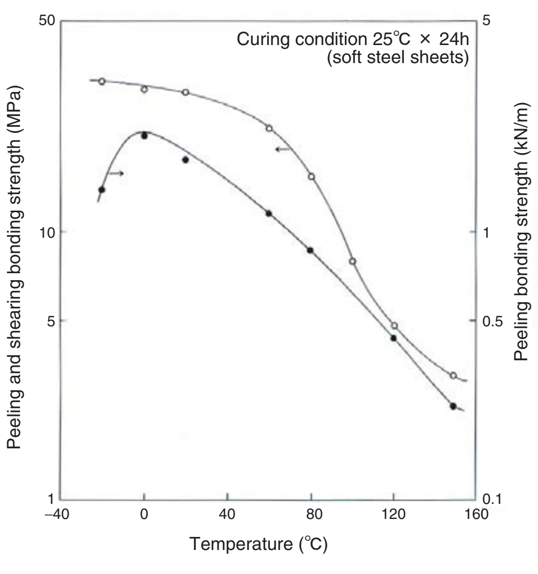

Figure 1. Temperature dependencies of bonding strength for ThreeBond 2087

Table 5. Adhesion performances of different materials for ThreeBond 2087

Adherend	Shearing bonding strength	Adherend	Shearing bonding strength
Hard vinyl chloride	2.9* { 30}	PPS	5.9 { 60}
6.6 nylon	2.0 { 20}	PET	5.8 { 59}
ABS	3.7 { 38}	Soft steel	26.0 {265}
Polyacetal	1.2 { 12}	Copper	24.5 {250}
Polystyrene	2.8 { 28}	Brass	24.5 {250}
PC	7.9* { 80}	Chrome-plated steel sheet	20.6 {210}
Acrylic	1.7 { 17}	Aluminum	24.5 {250}
Phenol	13.7* {140}	Stainless	24.5 {250}
FRP (Polyester)	11.8* {120}	Zinc-plated steel sheet	19.6 {200}

Curing condition 25 °C × 24 hours

Note: Material breakdown

(2) Epoxy elastic adhesives

Unlike existing room-temperature curing two-part epoxy adhesives, epoxy elastic adhesives are designed based on the new concepts of relaxing internal stress with adhesive layers to decrease adhesiveness deterioration with age and improve durability. These are flexible modified epoxy, because IPN is used for epoxy resins with flexible components. The elongation of cured objects is 100 - 200 %. Table 6 and 7 show the performances of epoxy elastic adhesives (ThreeBond 3951).

Table 6. Physical properties of cured objects for ThreeBond 3951

Hardness (shore A)	76
Peeling strength	7.8MPa { 80kgf/cm^2}
Elongation percentage	150%
Shearing bonding strength (Fe/Fe)	9.8MPa {100kgf/cm^2}
Peeling strength (Fe/Fe)	3.1kN/m {8kgf/25mm wide}
Volume resistivity	$3.0\times10^{13}\Omega$cm

Curing condition 25 °C × 7 days

Table 7. Bonding strength against different materials for ThreeBond 3951 MPa {kgf/cm^2}

Adherend	Shearing bonding strength	Adherend	Shearing bonding strength
Hard vinyl chloride	5.5 {56}	PPS	4.9* { 50}
6.6 nylon	4.2 {43}	PET	6.9 { 70}
ABS	7.2* {73}	Duranex	5.9 { 60}
Polystyrene	4.9 {50}	Soft steel	9.8 {100}
PC	5.9 {60}	Copper	6.9 { 70}
Polyester	8.8 {90}	Aluminum	10.8 {110}
Phenol	8.5 {87}	Stainless steel	9.8 {100}

Curing condition 5°C x 7 days

Note: Material breakdown

4-2. Modified acrylic, second-generation acrylic adhesives (SGA)

Acrylic structural adhesives are two-part adhesives which do not require blending. Fast curing can be caused only by applying an adhesive agent and an accelerator to each side of an object and bonding it with pressure. They offer approximately 5 minute set time (fixing time), 19.6MPa{200kgf/cm2} peeling and shearing strength, and more than 3.9kN/m{10kgf/25mm} T-type peeling strength equivalent to epoxy. Also, they are excellent in oily surface bonding, impact resistance, and durability.

We provide two-part base agent types (ThreeBond 3923/3928) and primer types (ThreeBond 3920B/3925B), but these have the disadvantage of acrylic monomer odor. Low odor adhesives also have been developed recently (ThreeBond 3921/3926, 3055/3097). Table 8 and 9 show the performances of second-generation acrylic adhesives (ThreeBond 3923/3928).

Table 8. Bonding strength of ThreeBond 3923/3928

Item		
Peeling and shearing strength	MPa {kgf/cm^2} Fe/Fe	26.5 {270}
Peeling strength	kN/m {kgf/25mm} Fe/Fe	2.8 { 7}
Peeling strength	kN/m {kgf/25mm} Al/Al	3.1 { 8}
Impact strength	J/m^2 {kgf•cm/cm^2} Fe/Fe	14.7 { 15}
Hot shearing bonding strength	–30°C	28.4 {290}
Mpa {kgf/cm^2}	25°C	26.5 {270}
Fe/Fe	60°C	15.7 {160}
	80°C	8.8 { 90}
	120°C	2.0 { 20}
	150°C	1.0 { 10}

Curing condition 25°C x 24 hours

Table 9. Materials and sharing bonding strength of different adherands (ThreeBond 3923/3928)

Unit: MPa {kgf/cm^2}

Material	Shearing bonding strength
Fe/Fe	26.5 {270}
Sus/Sus	23.5 {240}
Al/Al	16.7 {170}
Ni/Ni	18.6 {190}
Brass/Brass	18.6 {190}
Fe/Sus	21.6 {220}
Fe/Al	20.6 {210}
Fe/Ni	22.5 {230}
Sus/ABS	19.6* {200}
ABS/ABS	2.9 { 30}
Hard PVC/Hard PVC	9.8* {100}
Nylon/Nylon	1.0 { 10}
PC/PC	14.7* {150}
Acrylic/Acrylic	2.9 { 30}

Curing condition 25°C x 24 hours　　Note: Material breakdown

4-3. Anaerobiotic structural adhesives

Anaerobiotic structural adhesives are one-part room-temperature curing adhesives. While they do not harden during contacts with the air (oxygen), they polymerize and harden after the air is removed from the gap between metals. Redox polymerization initiators are compounded in radical polymerization acrylic oligomers and monomers. Anaerobic and UV curing adhesives containing photo polymerization initiators are also provided to harden an excess. The original application of these adhesives was mainly thread locking, but now they expand the area to include structural adhesives, and provide bonding strength equivalent to epoxy by using ultraviolet, primer, and heat.

The curing speed of anaerobiotic adhesives depends on the metal types. While they harden fast for active metals such as ferrum, copper, and aluminum, they harden slow for inactive metals such as plated surfaces. Figure 2 and 3 show the bonding strength durability of UV-curing anaerobiotic structural adhesives (ThreeBond 3065/3096).

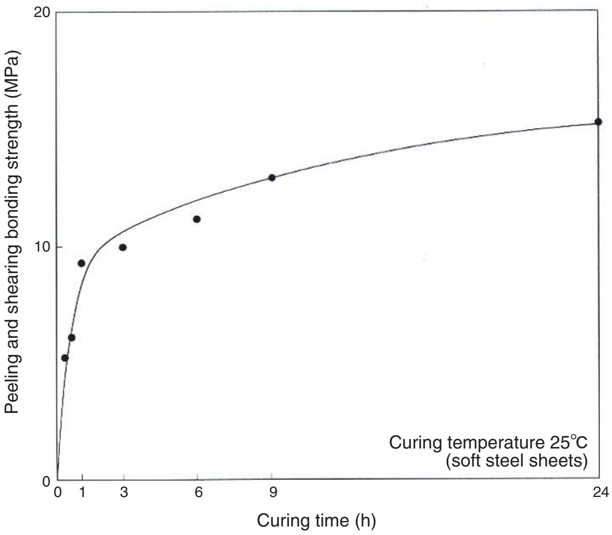

Figure 2. Curing speed of ThreeBond 3065/3096

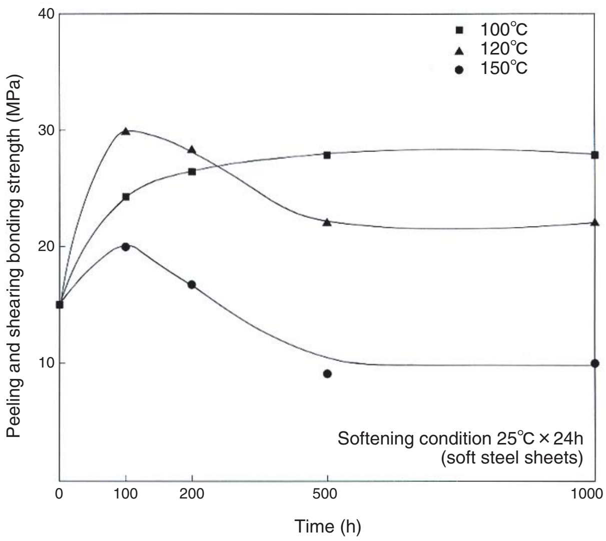

Figure 3. Heat aging of ThreeBond 3065/3096

4-4. Cyanoacrylate

Cyanoacrylate is generally called instant adhesives. Cyanoacrylate causes anion polymerization using an initiator of small amount of moisture attached to an adherend surface and hardens instantly. The set time for ultrafast curing types is now less than 5 seconds (between soft steel sheets). These have many different types: impact resistance, high peeling adhesive strength (ThreeBond 1735), and low bleaching (ThreeBond 1721) types. Also, difficult-to-bond primers (ThreeBond 1797, 17X-050) such as polypropylene, polyacetal, and teflon, curing accelerators (ThreeBond 1796), and release agent (ThreeBond 1795) are provided. Even though the heat resistance grade is 130°C and the durability is poor, small components demand for these adhesives due to the fast curing and high strength properties. Figure 4 shows the heat resistances of high peeling adhesive strength cyanoacrylate (ThreeBond 1735). Also, Table 10 and 11 show the adhesion performances of difficult-to-bond materials.

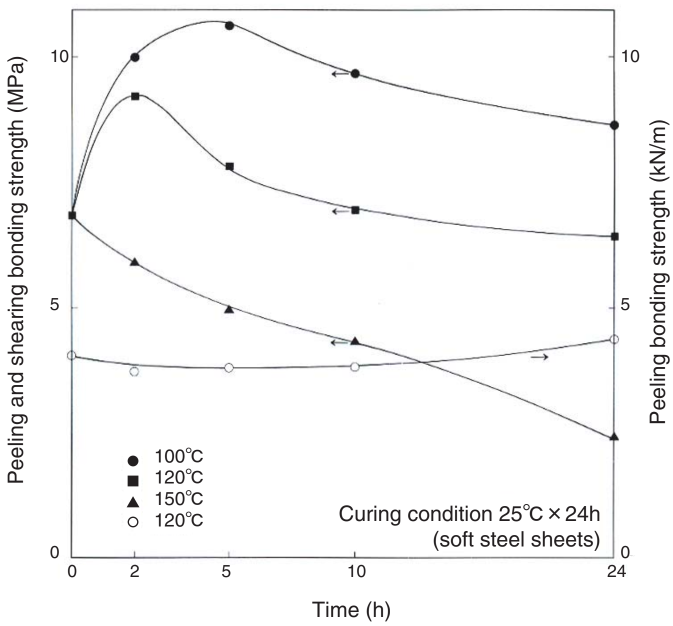

Figure 4. Heat aging of ThreeBond 1735

Table 10. Peeling and shearing bonding strength for ThreeBond 1797 MPa{kgf/cm^2}

Material \ Material	Polypropylene	Polyethylene	Polyacetal	Ferrum
Polypropylene	4.5* {46}	3.8* {39}	4.9* {50}	2.8 { 28}
Polyethylene	—	3.2 {33}	3.6 {37}	2.2 { 22}
Polyacetal	—	—	4.6 {47}	3.1 { 31}
Iron	—	—	—	12.8 {131}

Adhesives: ThreeBond 1741 Note: Material breakdown Curing condition 25°C x 24 hours

Table 11. Teflon bonding (ThreeBond 1741/17X-50)

Peeling and shearing bonding strength (teflon, t = 1mm)	0.95 MPa{9.7kgf/cm^2}

Curling condition 25°C × 24 hours

4-5. Urethane

Two-part room-temperature curing urethane adhesives composed of urethane prepolymers with isocyanate groups in the terminal and chemical compounds with active hydrogen groups provide excellent adhesion performances for plastics, and thus FRP structural adhesive grades have been brought to the market. The cured coatings have strength against peeling and impacts. However, due to their low heat resistances and poor adhesion performances to metals, they require primers to achieve extra-strength adhesiveness.

4-6. Silicone

Room-temperature curing (RTV) silicone adhesives include one-part and two-part adhesives. One-part adhesives are moisture-curing type hardened by condensation reaction, and they release acetone, oxime, acetic acid, and alcohol. Due to the metal corrosion problem, deacetone and dealcohol types are generally used, and they are limited to bonding small electronic parts because they are moisture curing. On the other hand, two-part adhesives are addition type capable of bonding large areas.

Silicone adhesives provide excellent heat resistances, cold resistances, and thermal conductances, but they do not have extra strength because of the low cohesion. Since the cured objects become rubber-like elastic solids, these adhesives are used to bond adherends having a large difference between thermal expansion coefficients. Table 12 shows the performances of one-component room-temperature curing silicone adhesive (ThreeBond 1220).

Table 12. One-component-based room-temperature curing silicone adhesives (ThreeBond 1220)

Uncured properties	Appearance	Fluid paste
	Color	White
	Viscosity Pa•s (P) (25°C)	50 {500}
	Dry to touch time•minutes (25°C)	5
Cured properties	Specific gravity (25°C)	1.04
	Hardness (JIS-A)	27
	Peeling strength MPa {kgf/cm^2}	2.6 {26}
	Elongation %	450
	Peeling and shearing bonding strength (glass) MPa {kgf/cm^2}	1.0 {10}
	Low molecular siloxane component share %	0.3
Electrical properties	Volume resistivity Ω•cm	8×10^{15}
	Dielectric breakdown strength kV/mm	34
	Permittivity 10^5Hz	2.7
	Dielectric tangent 10^5Hz	0.0006

5. Applications of structural adhesives and engineering adhesives

5-1. Applications of structural adhesives

Structural adhesives are used to bond automobile parts such as disc pads and clutch facings in addition to structural components for aircrafts.

(1) Structure bonding of honeycomb sandwich structural bodies

Honeycomb cores are formed from many groups of hexagonal columns bonded with aluminum files, paper, plastics using adhesives, and their structure is faveolate. Therefore, they are lightweighted and typically have sandwich structures which are joined using adhesives with surface materials such as aluminium sheets and FRPs. They are widely used as lightweight structural components for aircrafts, rolling stocks, and building materials because they have extremely high strength and stiffness for their weight as well as heat exchange, thermal insulation, and impact absorption effects.

(2) Structure bonding for automobiles

Automobile industries have applied structural adhesives to join parts such as brake linings and headlights, and automobile assembling lines have used one-part epoxy adhesives which harden utilizing the heat of a furnace in the painting process in place of spot weldings. Also, adhesives for direct glazing are used to bond front, rear, and side windows, etc.

5-2. Applications of engineering adhesives

Engineering adhesives are widely used to bond and seal automobiles, electric appliances, electronics, office machines, medical equipments, building materials, furnitures, rolling stocks, optical equipments, and glass ceramics.

(1) Automobile DC motors: bonding housings including wiper and fan motor with magnets, fixing amateur coils.

(2) Small precision motors: bonding circuit boards of video and floppy motors with coils, bonding magnets and plastic magnets with yokes.

(3) Electrical and electronic components: fixing relays and terminals, bonding piezoelectric buzzers, bonding and sealing LCDs.

(4) Acoustic components: bonding speaker magnets, bonding voice coils, fixing lead wires.

(5) Optical equipments: bonding lenses and prisms.

(6) Medical equipments: bonding injection needles.

Conclusion

We described the types and performances of structural and engineering adhesives. Adhesive materials, compositions, and functions are improving every year, and we encounter the question how we can establish a trust with our customers who mainly use these structural adhesives.

The current research and development of adhesives focuses on improving bonding durability and reliability, increasing curing speeds, and providing nonpolluting and special features. From an overall perspective of bonding technology, to clear these issues, we also need to consider the reforms of surfaces and bonding process managements. The surface reform is extremely important for bonding stability, especially for bonding durability, and critical to the structure bonding technology. The research and development of structure bonding has been advancing also in Japan, and now we are about putting the results into practice. We are looking forward to the achievements.

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