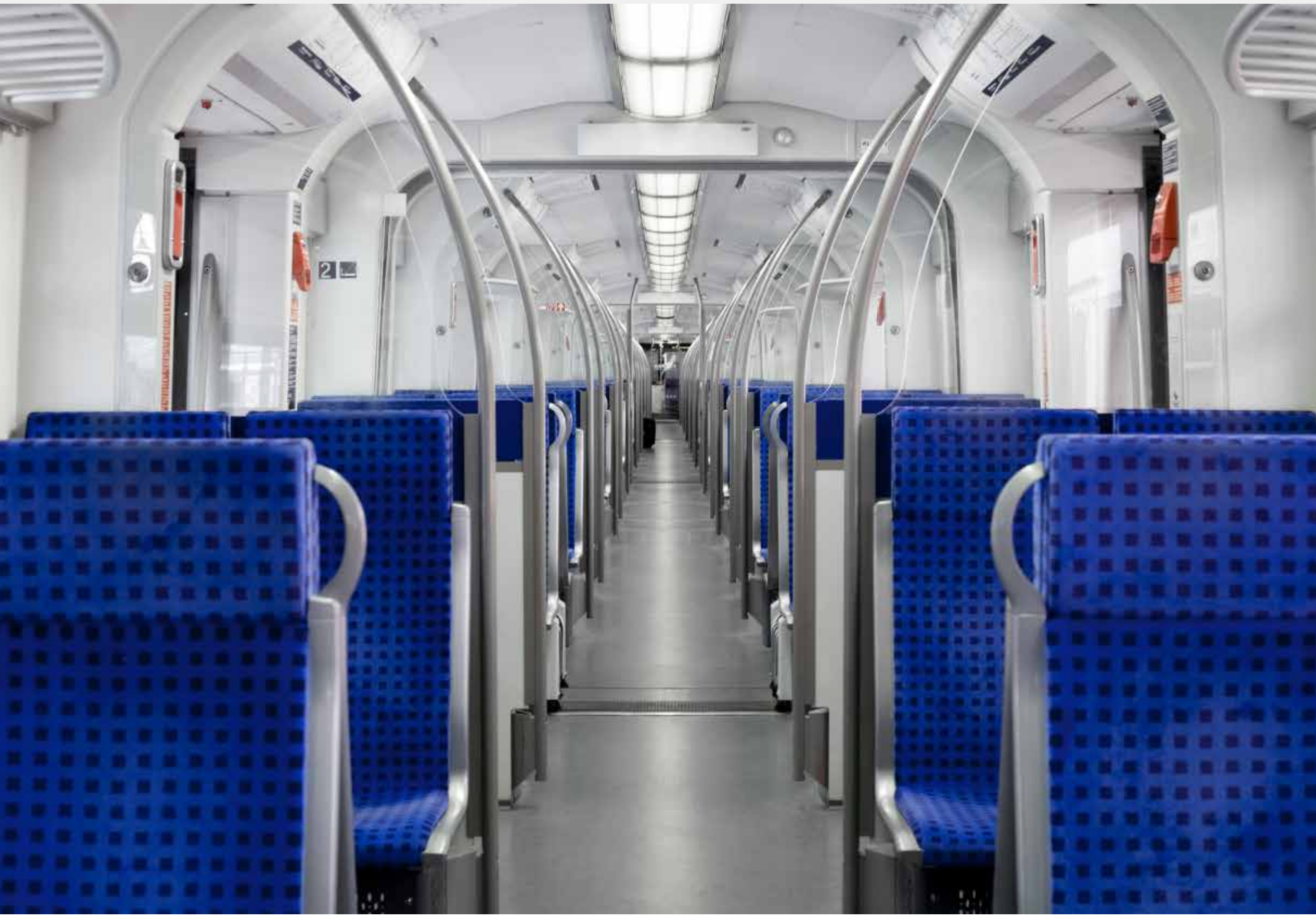

AN INTRODUCTION TO MMA STRUCTURAL ADHESIVES

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SCIGRIP's range of methyl methacrylate (MMA) structural adhesives has been developed to tackle the challenges of bonding metals, plastics and composites. Offering a combination of strength, toughness and ease of use, MMAs are proving their worth in numerous demanding applications in the marine, transportation, and building and construction industries. This article reviews the key features of MMA adhesives and highlights their benefits over other joining technologies.

There are a large number of adhesive types available in the marketplace which are suitable for various applications. The term 'structural adhesives' refers to adhesives that are designed to join two surfaces to form part of a load-bearing structure. The joints will have lap shear strengths of greater than 1 MPa and, typically, greater than 10 MPa. The most widely used structural adhesives are epoxies and polyurethanes; cyanoacrylates, and certain urethanes and acrylic adhesives, are also available. MMAs are a relatively newer technology and as such their properties and benefits are not yet as widely understood in the end user industries.

What are MMAs?

Scigrip's patented MMA adhesives consist of an adhesive resin component composed of methacrylate monomers, amines and additional rubbers and toughening agents, along with a peroxide-based activator paste (Figure 1).

When mixed, the peroxides react rapidly with the amines to release extremely reactive free radicals. The free radicals interact with a double bond in the methacrylate monomers leading to a very rapid and exothermic polymerisation reaction and the curing of the adhesive.

Key properties for a structural adhesive are strength, toughness and flexibility. The latter is particularly important when bonding dissimilar materials with high differential flexibilities, such as a rigid metal and a flexible plastic. The toughness and flexibility of an adhesive film depends on the rigidity and flexibility of the polymer and the crosslink density. Higher crosslinking leads to improved strength and chemical and heat resistance, but reduced flexibility (brittle bonds) and higher viscosity. Lower crosslinking leads to reduced chemical resistance and weaker bonds, but improved flexibility (bonds are less prone to cracking) and lower viscosity.

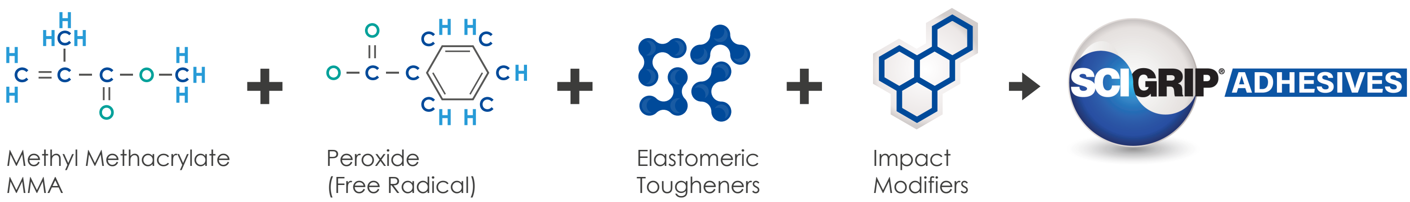

Figure 1: Scigrip MMA adhesives are formed by a free radical polymerisation mechanism which is highly exothermic

Epoxy, the highest strength adhesive available, has a high crosslink density, typical tensile strengths in the range of 27-36 MPa, elongation of 2-6% and Young's Modulus of 900-1400 MPa, while polyurethane has a lower crosslink density, tensile strengths of 6-14 MPa, and elongation of 100-300%. With a crosslink density between that of epoxy and polyurethane, Scigrip's MMA technology combines high strength with good flexibility as shown in Figure 2.

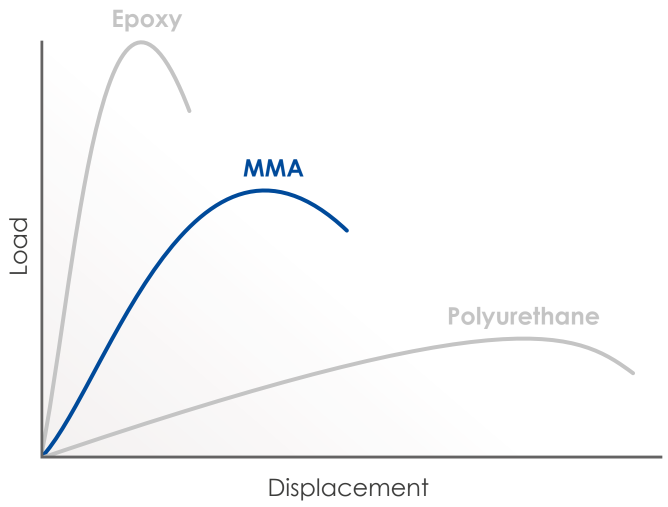

Figure 2: As this chart of load (strength) against displacement (elongation) illustrates, MMA technology bridges the gap between the tensile strength of epoxies and the flexibility of polyurethanes.

A unique advantage of MMAs is their ability to fully cure and reach their full strength (complete crosslinking) at room temperature, a result of the exothermic reaction by which they are formed. Other structural adhesives, including some two-part epoxies and polyurethanes, require the application of heat in order to obtain the same cure speed and to achieve their optimum properties. The fast exothermic reaction also means the period between cure and fixture time is very short for MMAs. This fast green strength gain for a given application time is considered one of the most valuable advantages of MMAs by many customers.

Another key benefit of Scigrip's MMAs is the large range of working times which is available to suit customers' different process requirements. This is achieved by adjusting the activator. Scigrip products offer working times ranging from 5 minutes up to 120 minutes, and fixture times of 6 minutes up to 4 hours.

Exothermic reaction - polymerisation

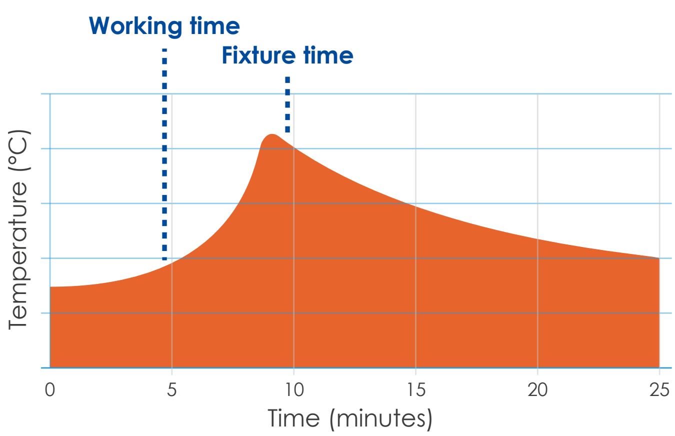

Figure 3: This graph of exotherm temperature vs time at room temperature shows the fast cure of an MMA adhesive.

As with most chemical reactions the ambient temperature does affect the working time of MMA adhesives because at higher temperatures the polymerisation reaction is quicker. In colder temperatures the products will take longer to cure, but they will still cure without the addition of heat. However, by changing the activator the working time can be adjusted to optimise productivity on warmer or cooler days. Figure 4 illustrates the effect of ambient temperature on working time.

Exothermic reaction - polymerisation

Heat speeds while cold holds the process

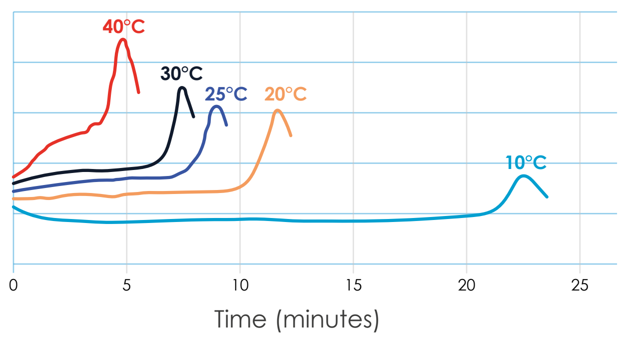

Figure 4: At higher ambient temperatures the working time for MMA adhesives is reduced.

Where to use MMAs

MMAs excel in bonding three key substrates:

- metals, including steel, stainless steel and aluminium;
- thermoset composites (both glass fibre and carbon fibre reinforced), including unsaturated polyester, vinyl ester, gel-coat, sheet moulding compound (SMC), phenolic and epoxy; and
- thermoplastics, such as acrylics, acrylonitrile butadiene styrene (ABS), polycarbonates and polyvinyl chloride (PVC).

Thermoset	Thermoplastic	Metal
Unsaturated polyester	Acrylics	Steel
Vinyl ester	ABS and blends	Stainless steel
Gelcoat	Polycarbonates and blends	Aluminium
Sheet moulding compound (SMC)	PVC (rigid & flexible)	Ecoated steel
Resin transfer moulding (RTM)	Styrenics	
Phenolic	Other engineered plastics	
Epoxy		

Figure 5: Key substrates for MMA adhesives.

Unlike other adhesives, when using MMAs far less surface preparation is required to achieve optimum bonding on metal, composite and plastic substrates. When using epoxies and polyurethanes more abrasion is required on all substrates and more cleaning and priming is necessary on many substrates. With the majority of MMAs only a solvent wipe is required to remove any light oils on metals and on composites just a dry wipe is needed. With many plastics only a dry wipe is required, while some will need a solvent wipe or abrasion.

Selected products in the Scigrip range can bond metals without the need for a primer. Cutting out this step makes production leaner and improves quality by avoiding potential priming errors. Composite components often require thick bond lines to cope with dimensional inaccuracies and Scigrip offers MMA products which enable bondline thicknesses up to 39 mm without boiling, which is a unique capability for a structural adhesive.

Scigrip is also developing products designed to meet the challenges of difficult-to-bond substrates such as polypropylene (PP), polyethylene (PE), SMC, dicyclopentadiene (DCPD) and galvanised steel. These substrates have low surface energy (LSE), which results in poor adhesive wet out of the surface. For optimum adhesion, an adhesive must thoroughly 'wet out' the surface to be bonded. This means the adhesive flows and covers a surface to maximise the contact area and the attractive forces between the adhesive and bonding surface.

For a liquid adhesive to effectively wet out a surface, the surface energy of the adhesive must be as low as, or lower than, the surface energy of the substrate to be bonded. Standard adhesive formulations wet out and bond high surface energy (HSE) substrates such as metal or ABS plastic, but fail to bond low surface energy polyolefins like PP and PE. While techniques such as plastic welding and friction welding are the current favoured systems for bonding PP and PE to themselves, they cannot be used to bond PP and PE to a different material. So while the competitive price of these plastics makes them initially very attractive to designers, the difficulties encountered when trying to bond them creates issues further down the production line. Scigrip is developing products to meet the challenges of creating high strength bonds on these low surface energy substrates.

Benefits over competitive technologies

The use of MMA structural adhesives can overcome the issues associated with the historic joining techniques of mechanical fasteners and welding, and they offer advantages over competitive adhesive technologies (Figure 6).

The use of mechanical fasteners is labour intensive, and the fasteners can corrode and loosen. The drilling of holes, and the stress areas that this creates, can weaken the underlying structure. Combining fasteners with substrates of a different material can lead to galvanic corrosion. And while it is possible to weld dissimilar materials together, this process is extremely expensive and labour intensive.

Epoxy adhesives have issues with bonding dissimilar materials because they are brittle, cannot conform to differential expansion and contraction and will therefore crack causing early bond failure under impact loading. They are also very sensitive to changes in mix ratios and are brittle when cured. MMAs are less brittle (less prone to cracking), easier to use (as mix ratios are not as critical), and offer large gap fill capability, choice of cure speed, low viscosity, and low VOC emissions.

Polyurethane adhesives have better fatigue resistance and impact resistance than epoxies but they contain isocyanates, a significant health and safety risk, and to obtain a fast cure they need to be heated. They are also sensitive to surface preparation and the substrate needs to be cleaned and, in many cases, primed. Priming adds another process, which can cause quality issues and premature failure to the structural application. MMAs have higher bond strength than urethanes and better impact and fatigue resistance. They also offer large gap fills, good chemical and environmental resistance, and fast cure speed. They are less sensitive to the environment (two-part polyurethanes require moisture to cure and therefore do not cure well in low humidity) and MMAs do not contain isocyanates.

Competitive Technology	MMA Benefits
Mechanical fasteners	Greater durability (mechanical fasteners can loosen/fail with time) Even distribution of stress over the entire bonded surface Less labour-intensive (increased productivity) Lower weight Corrosion-free Gap filling Better aesthetics (no protruding rivets etc.)
Welding	Far less expensive (no post finishing work required) Can be used with dissimilar materials Easier to use and less labour-intensive (increased productivity) Corrosion-free Better aesthetics (no distortion due to heat) Bonding difficult to access areas
Epoxies	Less brittle, less prone to cracking. Non-critical mix-ratios, easy to use. Large gap fill and choice of cure speed, adaptable.
Polyurethanes (PU)	High bond strength and good impact resistance Large gap fills, less sensitive to environment Good chemical and environmental resistance Fast cure speed Minimal health risks (non-isocyanate)
Pastes	High bond strength and impact resistance Choice of cartridges and bulk, easy to use

Figure 6: The benefits of MMA structural adhesives over competitive technologies.

Vinyl ester and polyester pastes are widely used in the marine and the composite markets. They are a low cost alternative to MMAs, but do not offer the same high bond strength and impact resistance. A high amount of surface preparation required, their fatigue resistance is extremely low, and they cannot be used to bond dissimilar materials. MMAs offer high bond strength and impact resistance, and ease of use.

The Scigrip range

Scigrip offers two MMA formulations – the established 1:1 range and the newer 10:1 range – and these offer very different performances. The numbers indicate the mix ratio. For example, 1:1 would mean 200 ml of Part A (adhesive) to 200 ml of Part B (activator). The 1:1 adhesives have higher strength than the 10:1 products, but lower elongation.

The Scigrip 1:1 range – the SG5000 Series – consists of four products, offering working times ranging from 2 up to 45 minutes . They offer maximum tensile strengths of 35-40 MPa and maximum tensile elongation of 5-10%. These products are ideal for bonding substrates of aluminium, steel, PVC, fibre reinforced plastic (FRP)/glass reinforced plastic (GRP), ABS, acrylics, and polycarbonates.

They have some restrictions. Highly dissimilar materials (e.g. mild steel and ABS), with different rates of thermal expansion and contraction, can be an issue for these products when bonding long substrates longer than 500 mm together. The low elongation values of the adhesive lead to reduced ability to flex when the difference in expansion and contraction is large. This effect is greater for larger bond areas and can result in adhesive failure. These adhesives are also not ideal at large bond gaps (greater than 5 mm) as the high exothermic heat they generate tends to form discoloration and surface distortions on thin substrates.

One important factor to consider when designing a joint is that bond strength decreases as bond thickness increases. The maximum recommended bond thickness of Scigrip 1:1 products is 2 mm.

Scigrip's 10:1 products offer tensile strengths around 4-5 MPa lower than 1:1s, but higher elongation at 30-150%. The range incorporates a number of specialised products.

SG100 Series Bright White UV Resistant Adhesive is ideal for marine applications and recreational vehicles (RVs). It is UV resistant and offers a long-lasting white colour and excellent fatigue, impact and shock load resistance. SG230 is also especially suited to the marine industry and it has been formulated to enable a large gap filling capability of up to around 39 mm. All other adhesive technologies will boil at this thickness, which will weaken the bond. This product also offers long working times of up to 130 minutes and high sag resistance on vertical surfaces. It has marine approvals from Lloyds, ABS (American Bureau of Shipping) for use on metals, thermoplastic and thermoset composites. These products are suitable for bonding to polyester, epoxy, vinyl ester and phenolic resin matrix.

SG300 is a primer-less metals bonder which creates a corrosion-resistant bond. It will provide corrosion resistance above and beyond any paint system and resolves any galvanic corrosion issues. Unlike epoxies, which require abrasion of the substrate when bonding aluminium, mild steels or metals, SG300 has no requirements for abrasion other than on mild steel. On mild steel abrasion is only required to remove any minute surface corrosion that may have taken place prior to bonding. On aluminium MMAs will key through the oxidised layer of aluminium better than any other adhesive technology. SG300 has Paccar, FST (fire, smoke and toxicity requirements for interior rail assembly) for European and Chinese rail car manufacturers, Lloyds and ABS approvals.

SG600 is a multi-purpose plastics bonder, which does need priming on metals. Ideal for certain plastics, such as ABS, that typically suffer from stress cracking with many adhesive technologies, it does not affect the overall performance of the plastic.

The 10:1 range also includes a high temperature resistant product and a formulation designed for use with low surface energy plastics.

Application areas

The properties of Scigrip's MMAs adhesives are already being exploited in the marine, transportation, wind energy and building and construction industries.

In the marine sector MMAs offer working times to suit all boat builders. Typical application areas include bonding hulls, deck liners, ski boats, yachts, internal fixtures, canoes and kayaks.

In the rail, bus and truck industries, fatigue-resistant composite to metal bonding is required and applications for MMAs include bumpers, lighting fixtures, wheel arches, roof panels and internal fixtures. Other important markets are recreational vehicles, which MMAs offer high strength and toughness, and agricultural vehicles, where heavy duty metal to plastics bonding with minimal surface preparation is required.

In the bonding of wind turbine blades MMAs offer long open time and large gap fill without overheating. Currently the more established epoxy technology is widely used in this area but with epoxies it is necessary to wait until the GRP surface is stabilised (no styrene) and then the surface needs to be cleaned and abraded. The epoxy adhesive also needs to be post-cured to enable complete crosslinking.

In the building and construction sector applications for MMAs include uPVC doors, signs and displays, and architectural components.

Scigrip offer a wide range of packaging options to meet the demands of the global market and diverse manufacturing requirements. Scigrip MMAs are available in cartridge and bulk format, with standard packaging ranging from 50 ml up to 189 litres for high volume production runs. All products have GREENGUARD Certification, which means they meet some of the world's most rigorous standards for low emissions of volatile organic compounds (VOCs) into indoor air.

New developments

Customers' demands for new application processes, new substrates and assembly performance, as well as improved productivity are key areas of focus for Scigrip's experienced R&D team. The bonding of dissimilar materials and new substrates are challenges it routinely addresses. Recent developments include SG800, a 10:1 MMA offering temperature resistance up to 121°C, PPX5 Ultimate Plastic Bonder, which can achieve bonding on low surface energy plastics such as PP, and SG6000, which has been developed to bond DCPD and SMC substrates with no surface preparation.

Adhesives terminology

Boiling: When the exothermic reaction is so high that it causes bubbling of the adhesive.

Bond line: The layer of adhesive which attaches two surfaces.

Bond line read through: A visible distortion of the substrate over a cured adhesive bond line, primarily resulting from a difference in the exothermic heat and shrinkage of the adhesive during cure.

Cure: To develop the strength properties of an adhesive by chemical reaction.

Crosslink: To form chemical bonds between molecules to produce a three-dimensional network.

Elongation: A measure of the ductility of a material, or the amount of strain it can experience before failure in tensile testing. Defined as the strain in a tensile test, this is measured as the amount of deformation (final length to original length) before a sample breaks.

Young's Modulus or Elastic Modulus: A measurement of elasticity (recoverable stretch) determined by the ratio of stress to strain. This is usually measured by tensile testing.

Fixture time: The time taken to reach the point at which the adhesive sets firm. Scigrip defines this as the time to achieve 70-80% of the ultimate strength in shear for an aluminum to aluminum bond.

Free radical polymerisation: A key synthesis route for a wide variety of polymers in which a polymer forms by the successive addition of free radical building blocks. Free radicals can be formed via a number of different mechanisms usually involving separate initiator molecules. Following its generation, the initiating free radical adds monomer units, thereby growing the polymer chain.

Gap filling: An adhesive capable of forming and maintaining a bond between surfaces that are not close-fitting.

Galvanic corrosion: An electrochemical process in which one metal corrodes preferentially to another when both metals are in electrical contact, in the presence of an electrolyte.

Post cure: When an adhesive assembly is exposed to an additional cure, following the initial cure, for the purpose of modifying specific properties.

Primer: A coating applied to a surface, prior to the application of an adhesive, to improve the chemical adhesion of the product to the substrate.

Sag: The gravity-induced downward flow of an adhesive when applied on a vertical surface.

Working time: The length of time an adhesive can be worked with before it starts to cure. This includes working time in nozzle, time to apply and time to clamp parts. It is measured as the time to reach 41°C (90°F), which is the point at which the polymerisation reaction increases exponentially. Parts not bonded correctly within the working time are at risk of early adhesive failure.

About SCIGRIP

SCIGRIP Smarter Adhesive Solutions is a wholly owned subsidiary of IPS Corporation, a dedicated, successful adhesives manufacturer for over 65 years. This depth of experience has resulted in an organisation that is consistently creating new adhesive chemistries and bonding solutions. SCIGRIP offers cutting edge formulations of methacrylate adhesives that are unrivalled for their combination of strength, toughness and ease of use. With the recent acquisition of Holdtite Adhesives, SCIGRIP has added anaerobic, cyanoacrylate and UV cure adhesives to its portfolio of high quality products.

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