

Photoinitiated Cyanoacrylates for Fast Underwater Bonding

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Synopsis

Photoinitiated Cyanoacrylates for Fast Underwater Bonding

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SYNOPSIS

Strong underwater bonds between polycarbonate sheet and various other substrates were achieved using ethyl 2-cyanoacrylate gel cured with an anionic photoinitiator (dibenzoylferrocene). The gel reacts quickly with water on contact and forms a protective polyethyl cyanoacrylate (PECA) skin. This provides a diffusion barrier that protects the inner monomer from further reaction with or polymerisation by water (hydroxide ions). The PECA skin is, however, permeable to water and the inner monomer slowly reacts as water diffuses through the PECA skin.

The application procedure for this adhesive is critical because of the fast reaction with water. It is recommended that the adhesive be applied at the centre of the bond area in such a way as to cover the smallest exposed surface area and that it should not be spread out over the entire surface area. The PECA skin will rupture when the substrates are pressed together, exposing unreacted monomer to the fresh new surface between the two substrates. The adhesive displaces water as it propagates towards the joint edges. In this way it is able to form a strong underwater bond.

Without a photoinitiator, ethyl cyanoacrylate adhesives will form strong bonds to smooth underwater surfaces. The addition of a photoinitiator (dibenzoylferrocene), however, increases the rate at which the bond strength develops. This can happen





within seconds following exposure to light. Photo differential scanning calorimetric (photo-DSC) analysis was used to determine the optimum photoinitiator concentration. A concentration of between 0.3% (m/m) and 0.1% (m/m) was found to be optimum for adhesive films between 0.5 and 1.2 mm thick.

Epoxy-based underwater adhesives have the disadvantage that the cure rate is very slow at low water temperatures. In contrast, the current system features a negative temperature dependence. Therefore, the curing rate is faster at lower water temperatures, making it highly suitable for very cold environmental conditions.

The underwater bonding properties of cyanoacrylate adhesive were measured on a wide range of metallic and non-metallic materials. Bond strengths ranged from 1 to 5 MPa respectively. The bond strength to polymer substrates (polycarbonate (PC), polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), fibre-reinforced polyester (FRP) and acrylonitrile / butadiene / styrene (ABS)) were much higher than those achieved to metals (carbon steel, aluminium, stainless steel 304 and anodised aluminium).

Bond strength (0.2 mm film thickness) develops in a very short time (less than a minute) using a 5 mW/cm² blue LED light source as trigger for the photo initiator. Water temperatures between 1.5 and 40 $^{\circ}$ C did not in fluence the ultimate bond strength achieved following 50 seconds of illumination.

The reduction in bond strength due to the ethyl cyanoacrylates reacting with water was measured in artificial sea water and potable water. A 20% reduction in bond strength was found after 10 minutes of water exposure. The underwater bond should therefore be made as soon as possible following exposure to water.

Bond ageing studies on both steel and polycarbonate showed an initial decrease in bond strength (during the first 50 hours); thereafter the bond strength stabilises.

Keywords: Ethyl cyanoacrylate, dibenzoylferrocene, photoinitiator, underwater bonding, photo differential scanning calorimetry



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NOMENCLATURE

5	
Area or overall frequency factor	mm ²
Acrylonitrile / Butadiene / Styrene	-
Alternating current	V
American Society for Testing and Materials	-
Attenuated Total Reflectance Infrared Spectroscopy	-
Benzoylferrocene (see Appendix E for structure)	-
Benzoylferrocene derivative (see Appendix E for structure)	-
Benzoylferrocene derivative (see Appendix E for structure)	-
Bisphenol A diglycidyl ether dimethacrylate	-
Cyanoacrylate	-
Council for Scientific and Industrial Research	-
Charge transfer to solvent	-
Density	g/cm ³
Direct current	V
Diphenylolpropane	-
Dibenzoylferrocene (see Appendix E for structure)	-
Dibenzoylferrocene derivative (see Appendix E for	-
structure)	
Dibenzoylferrocene derivative (see Appendix E for	-
structure)	
Dibenzoylferrocene derivative (see Appendix E for	-
structure)	
Dibenzoylferrocene derivative (see Appendix E for	-
structure)	
Dibenzoylferrocene derivative (see Appendix E for	-
structure)	
Differential scanning calorimetry/calorimeter	-
Overall activation energy	kJ/mol
Ethyl cyanoacrylate	-
	Area or overall frequency factor Acrylonitrile / Butadiene / Styrene Alternating current American Society for Testing and Materials Attenuated Total Reflectance Infrared Spectroscopy Benzoylferrocene (see Appendix E for structure) Benzoylferrocene derivative (see Appendix E for structure) Bonci for Scientific and Industrial Research Charge transfer to solvent Density Direct current Diphenylolpropane Dibenzoylferrocene derivative (see Appendix E for structure) Dibenzoylferrocene derivative (see Appendix E for structure)

Nomenclature

Photoinitiated Cyanoacrylates for Fast Underwater Bonding

ECH	Epichlorohydrin	-
Fc	Ferrocene (see Appendix E for structure)	-
Fe	Iron	-
FRP	Fibre-reinforced polyester (fibreglass)	-
FT-IR	Fourier transform infrared spectroscopy	-
h	Hours	
HQ	Hydroquinone	-
IN	Excited state	-
k	Rate constant	-
LED	Light emitting diode	-
LMCT	Ligand-to-metal charge transfer	-
m	Mass	g
mA	Current (milliampere)	-
MLCT	Metal-to-ligand charge transfer	-
MSA	Methanesulphonic acid	-
MSDS	Material safety data sheet	-
NCS	Thiocyanate Ion	-
NMISA	National Metrology Institute of South Africa	-
NSR	North Sea Resin	-
Nu⁻	Nucleophilic species	-
PBAN	Polybutadiene-co-acrylonitrile	-
PC	Polycarbonate	-
PECA	Polyethyl cyanoacrylate	-
PET	Polyethylene terephthalate	-
PI	Photoinitiator	-
PMMA	Polymethyl methacrylate	-
PVC	Polyvinyl chloride	-
R	Gas constant (8.314 J/mol. K)	J/mol. k
RH	Relative humidity	-
SDTA	Single differential thermal analysis	-
S	Seconds	-
t	Time	sec.
TEGDMA	Triethylene glycol dimethacrylate	-

Nomenclature

Photoinitiated Cyanoacrylates for Fast Underwater Bonding

TGA	Thermogravimetric analysis	-
TUT	Tshwane University of Technology	-
UV	Ultraviolet	-
UV-Vis	Ultraviolet – Visible	-
V	Volume or Voltage	mm ³
W	Work of adhesion	MJ/m ²
XRD	X-ray diffraction	-

Subscripts and Superscripts

А	Air	-
а	Activation	-
С	Centroid	-
dis	Disappearance	-
excit	Excitation	-
h	Planck's constant	-
ind	Induction	-
L	Liquid or Ligand	-
m	Order of dependence on converted fraction (α)	-
max	Maximum	-
n	Repeat units or order of dependence on unconverted	-
	fraction $(1 - \alpha)$	
р	Peak	-
therm	Thermal	-
х	x direction	-
xL	Liquid in x direction	-
ху	xy direction	-
у	y direction	-
уL	Liquid in y direction	-

Greek Alphabet

λ _{0.5}	Bandwidth at 50% intensity (Lambda)	nm
Δ	Difference (Delta)	-
φ	Disappearance quantum yield	-

Nomenclature

UNIVERSITEIT VAN PRETORIA UNIVERSITY OF PRETORIA YUNIBESITHI VA PRETORIA Photoinitiated Cyanoacrylates for Fast Underwater Bonding

8	Extinction coefficient (epsilon)	M ⁻¹ .cm ⁻¹
α	Fraction of the monomer converted (alpha)	-
υ	Frequency	Hz
μ	Micro (Mu)	10 ⁻⁶
τ	Shear strength	Ра
γ	Surface free energy	MJ/m ²
θ	Viewing angle (theta)	0
λ	Wavelength of light (lambda)	nm

CHAPTER 1 INTRODUCTION

This chapter gives a brief background on Fthe requirements for underwater adhesives and categorises these adhesives according to their properties and uses. A problem area is identified and the research objectives to address this problem are described.

1.1 Background

There is a need for underwater adhesives for bonding various underwater substrates. The physical properties required of these adhesives will depend on their specific application (Herman, 1976: 255). The specific adhesive categories refer to the following applications:

Category 1:

In harsh sea conditions or difficult underwater working environments, the time available for bonding may be limited due to strong currents and wave motion. In this type of application very rapid-curing adhesives are required. High bond strength is not always required, such as for attaching tags to rocks of geophysical interest (Foley *et al.*, 2001).

Category 2:

Underwater construction and repairs are normally done in calm water conditions requiring an adhesive with a high bond strength. The rate of curing should be fast enough to be viable, but does not need to be instantaneous as with a Category 1 adhesive. Typical work sites can include pits, sumps, underwater supports, boats, piers and pilings (Oman, 2003). This type of adhesive is required to protect the structure and should withstand attack by water over long periods of time.

It should also be remembered that the curing rate can be influenced by the water temperature and may vary greatly from location to location (Herman, 1976: 255)



Underwater adhesion has long been a formidable challenge to scientists, and has forced them to look at nature's underwater adhesion specialists in the form of barnacles and mussels. Barnacles and mussels secrete an adhesive protein that allows them to attach themselves rapidly to underwater structures. More detailed understanding of the properties and applications of these adhesive proteins may contribute significantly to progress with the formulation of underwater adhesives, and may have great medical and dental applications (Khandeparker & Anil, 2007). However, whether these adhesive proteins will produce affordable and commercially viable underwater adhesives with superior properties is not known (Waite, 1987) and, for the present, synthetic adhesives will have to suffice.

Synthetic adhesives generally fail because of a number of contributing factors (Herman, 1976):

- A thin film of water on the substrate surface prevents the adhesive from wetting the surface.
- The adhesive's components dissolve in water.
- The adhesive floats away from the substrate surface.
- Various adhesive monomers polymerise instantaneously on contact with water.
- Various monomers react too slowly to be of practical use.

The factors affecting adhesive joints underwater are discussed in more detail in Section 2.6.

1.2 Problem Statement

There is a need for an adhesive to rapidly bond metal and non-metal objects underwater with significant strength, in harsh and unusual conditions and, in particular, in water temperatures approaching 0 °C. The underwater surface may be rough or uneven, but should be free from any loose debris.

1.3 Development Objectives

The purpose of this investigation was to develop a technical process for fast underwater bonding of substrates. A key issue was to determine whether



cyanoacrylate (CA) adhesives cured by visible radiation can be used for very fast underwater bonding. The following properties of this radiation-cured cyanoacrylate adhesive were determined:

Using differential scanning calorimetry (DSC-7):

- the optimum concentration of photoinitiator for the bond line thickness
- the effect of temperature on polymerisation rate.

Using thermogravimetric analysis (TGA):

- the amount of filler to be added to cyanoacrylate gel
- the rate of evaporation of cyanoacrylates.

Using an Instron tensile testing instrument, the following effects on the shear bond strength:

- illumination time
- different substrate materials
- water temperature
- underwater work time (water polymerisation rate)
- water ageing of bonds.

This dissertation focuses on Category 1 adhesives, which require a fast curing rate but do not necessarily require very high bond strength.

Owing to the practical emphasis of this study, not all the scientific issues have been considered in detail. Rather, the focus was on developing a system based on commercially available materials.

CHAPTER 2: LITERATURE BACKGROUND

This chapter provides a basic overview of the small number of adhesives used for underwater bonding. Its gives the advantages of radiation-curing adhesives, and discusses the characteristics of the photoinitiator (dibenzoylferrocene) used to photo cure cyanoacrylate adhesives. The curing mechanism and the effect of moisture on cyanoacrylate adhesives are also discussed. Finally, it is explained how photo differential scanning calorimetry (photo-DSC) can be used to determine the kinetic nature of radiation-curing adhesives.

2.1 Adhesives for Underwater Bonding

There are a number of commercial adhesive products that can be used underwater. Although the formulation of these adhesive products may differ, the adhesives are mostly based on the following functional groups:

- epoxy adhesives
- acrylate adhesives.

Cyanoacrylates are classified as acrylate adhesives but have such unique characteristics that they are discussed separately. Cyanoacrylates are not really known as underwater adhesives but have been used underwater in several interesting applications.

Three adhesive types are discussed in the next sections.

2.1.1 Epoxy adhesives

Epoxy adhesives are excellent underwater adhesives. They are two-component systems: one part being the polyamine or polyamide curing agent, and the other part an epoxy resin. There are several patent holders for underwater epoxy adhesives, namely Cassutt & Messerly (1981), Drisko & Crilly (1975), Morris & Erickson (1982) and several others.

The epoxy resin is based on the reaction between diphenylolpropane (DPP), also known as Bisphenol A, and epichlorohydrin (ECH) and can be represented by the general formula in Figure 1.



Figure 1: Chemical structure of epoxy resin

(From Potter, 1970: 9-10)

The molecule is a linear molecule with two terminal epoxide groups at the points and secondary hydroxyl groups occurring at regular intervals along the length of the molecule. Aromatic rings make up a large part of the backbone of the chain. The degree of polymerisation (n) is essentially dependent on the ratio of ECH:DPP used during synthesis. The number of repeating units is used to control the viscosity of the resin. Commercially available epoxy resins are syrupy, viscous liquids curing to hard, brittle solids at room temperature (Potter, 1970: 9-10).

This type of adhesive has excellent mechanical properties and is corrosion resistant to many chemicals. Epoxy-based paints offer good corrosion protection and are therefore used in harsh environments such as the sea (Dhanalakshmi *et al.*, 1997, and Husain *et al.*, 2004). The adhesive is used mainly as a repair material for offshore structures. Repairs to steel (Bowditch *et al.*, 1986), wood (Lopez-Anido *et al.*, 2004) and concrete (Moksnes, 1981; Frigione *et al.*, 2005 and El-Hawary, 1998) using different epoxy materials in combination with fibre-reinforced polyesters (FRPs) have become a popular way of rehabilitating or renewing offshore structures, dramatically increasing the service life of such structures.

The secret to using epoxy resins in harsh underwater environments lies in the curing agents. In harsh environments, the preferred curing agent is a ketimine (ketone-blocked amine), which hydrolyses on contact with water to release a free amine (see Figure 2), which then reacts with the epoxy resin (Dhanalakshmi *et al.,* 1997).



$$\begin{array}{c} \mathsf{CH}_{3} & \mathsf{O} \\ \mathsf{I} \\ \mathsf{RN=C-CH}_{2}\mathsf{CH}_{3} + \mathsf{H}_{2}\mathsf{O} & \checkmark \\ \mathsf{(Ketimine)} & \mathsf{R-NH}_{2} + \mathsf{H}_{3}\mathsf{C-C-CH}_{2}\mathsf{CH}_{3} \end{array}$$

Figure 2: Ketimine hydrolysed on contact with water

(From Dhanalakshmi et al., 1997)

Epoxy adhesives fall into Category 2 type adhesives as classified above in Section 1.1. The reasons why epoxy adhesives will not perform as Category 1 adhesives are:

- These adhesives consist of two components and therefore have to be mixed. Mixing is time-consuming and difficult to do underwater.
- The cure rate of epoxy adhesives is affected by temperature and the curing rate becomes extremely slow at low temperatures.

2.1.2 Acrylate adhesives

Angelovici *et al.* (1990) developed a two-part toughened acrylic adhesive for underwater bonding. Different substrates were bonded at low temperature in a relatively short time. The acrylate adhesives showed good endurance following 8 months' exposure to sea water.

The development of the acrylate monomer 2,2-Bis[4-(2 hydroxy-3-methacryloyloxy propoxy) phenyl] propane, or Bisphenol A diglycidyl ether dimethacrylate, usually termed BisGMA, was a major step in the development of dental resins (Sandner *et al.*, 1997). These resins are required to bond to relatively wet surfaces (dentists try to dry the tooth as much as possible to improve adhesion) in a short time and to withstand long-term exposure to aqueous environments. The resin is mostly photopolymerised using a photoinitiator that reacts with either ultraviolet (UV) or visible light.

Various light sources are available, but blue light-emitting diode (LED) light sources have become popular for their long life, durability and low power consumption. LED



Literature background

light sources generate minimal heat and therefore do not require cooling fans with their associated noise and power consumption (Tsai *et al.*, 2004).

BisGMA has a high viscosity caused by hydrogen bonding between the hydroxyl groups in the alkyl chain (see Figure 3). This is a disadvantage because diluent monomers (triethylene glycol dimethacrylate (TEGDMA)) need to be added to get the dental resin into an easily workable viscosity (Sandner *et al.*, 1997).



Figure 3: Chemical structure of BisGMA (From Sandner *et al.*, 1997)

The hydrophilicity of both BisGMA and TEGDMA is the factor that causes their mechanical properties to deteriorate in aqueous environments (Sandner *et al.*, 1997).

Many improvements to dental composites have been made, such as the synthesis of new BisGMA chemical derivatives and the use of other acrylate monomers, such as low-viscosity aromatic dimethacrylates and urethane dimethacrylates.

Dolez *et al.* (2001 and 2003) used the same monomers employed in dental composites to develop an underwater light-cured acrylate adhesive. The principal monomer is BisGMA with several viscosity modifiers, including TEGDMA. Their underwater usage calls for very short bonding times at low temperature (Dolez *et al.*, 2000) in severe environmental conditions. A light-induced curing process was chosen as this is one of the fastest ways to cure polymers. The photoinitiator is camphorquinone, which has a major absorption peak at 468 nm, and therefore a blue LED light source (470 nm) can be used to cure the resin. This photopolymerisable acrylic system shows good properties as a potential fast-curing underwater adhesive.

A commercial acrylate adhesive cured underwater by blue light can be found under the trade name North Sea Resin (NSR, 2007). The resin can be used as a filler and sealant for most metals and plastics. When used as an adhesive, NSR must have a underwater surfaces.



clear top substrate or fibreglass mesh for light to reach the bonding area. The product can be used to perform emergency repairs to pipes, watercraft and other

Next we will look at an acrylate adhesive, cyanoacrylate or Superglue[™], that is not normally associated with underwater usage but is reported to form strong underwater bonds (Leonard & Brandes, 1975 and Card & West, 1988a; 1988b).

2.1.3 Cyanoacrylate adhesives

Superglue[™] is the trade name for cyanoacrylate (CA), an acrylate resin that rapidly polymerises, joining the bonded surfaces. It is mostly the cyanoacrylates of methyl, ethyl, butyl and octyl alkyl groups that are used as adhesives.

The adhesive properties of CA were first discovered by Harry Coover at Eastman Kodak during World War II. Coover soon discovered that this new adhesive will bond virtually any material available in seconds. It was finally marketed in 1958 as 'Superglue[™]' and is known for its quick bonding of a diverse range of substrates (Hayes, 2004). Methyl and ethyl cyanoacrylates are mostly used as general-purpose adhesives and are now readily available in any hardware or general store.

Cyanoacrylate is a thin-layer adhesive that only polymerises in thin layers when squeezed between the substrate surfaces. The adhesive is available in a gel form that has gap-filling properties. It is known to bond skin extremely fast because of the moisture and amino acids present on the skin. For this reason, cyanoacrylate adhesive was used for wound closure during World War II. It is, however, toxic to the body and forms formaldehyde upon polymerisation on the skin. To reduce the toxic effect of cyanoacrylate adhesive, a longer alkyl group was substituted for the acrylate. A four to eight carbon chain (butyl to octyl) added to the acrylate causes the adhesive to be less toxic by decreasing the polymerisation rate, thus giving the body a chance to rid itself of the toxic formaldehyde from the wound.

Liquid cyanoacrylate adhesives are not recommended for use underwater because of their rapid polymerisation with even the smallest amounts of moisture. However, the



adhesive seems to find interesting underwater uses such as the tagging of sea mammals (Mate *et al.*, 2007) and of mussels or scallops (Lemarié *et al.*, 2000 and Ross *et al.*, 2001), as well as for fixing coral to rocks underwater. Several patents describe the use of cyanoacrylate adhesives underwater – one patent by Leonard & Brandes (1975) and two by Card & West (1988a and 1988b). In the light of the extensive use of cyanoacrylates for medical (Davis *et al.*, 2001) and dental use in wet/moist environments (Bishara *et al.*, 2001), it was decided to investigate cyanoacrylate adhesive for underwater application. Underwater adhesion is accomplished by using a gel (or filled) adhesive and not the thin liquid.

The patent held by Leonard & Brandes (1975) uses a $CaCO_3$ and SiO_2 filler to make the cyanoacrylate adhesive into a paste. The paste can be applied underwater and is used to bond smooth underwater surfaces.

The patents by Card & West (1988a and 1988b) disclose a high-viscosity cyanoacrylate adhesive "gel^a". It is believed that polymerisation of the gel surface is so rapid upon submersion in water that the adhesive is encapsulated by a thin polyethyl-2-cyanoacrylate skin. The thin encapsulating skin is easily ruptured between the two substrate surfaces, exposing a new adhesive layer to the almost water-free mating (bonding) surface. Card & West (1988a) also make use of a surface-conforming material to minimise gap thickness on uneven and rough surfaces. In addition, they report that cyanoacrylate adhesives can bond underwater at very low temperatures (Card & West, 1988b).

This dissertation will focus on photoinitiated cyanoacrylate adhesive gel for use underwater. In this adhesive formulation the standard moisture-curing mechanism will ensure adhesion on the mating surface where gap thickness is a minimum, and the

^a A gel is actually a solid but the term is commonly used in technical literature for a thixotropic material. These materials normally have high viscosity and are solids under zero shear conditions. When sheared, the material's internal structure breaks down and the material is able to flow. The viscosity of thixotropic materials decreases over time under continuous shear, but recovers rapidly when shearing ceases. These gels find application in non-drip paints.



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auxiliary light curing mechanism will polymerise the adhesive well into gaps on the rough and uneven underwater surface.

Cyanoacrylate adhesives fall into Category 1 type adhesives as classified above because the curing rate is very fast, but bond strength may also deteriorate very fast depending on the substrate bonded.

2.2 Radiation Curing Adhesives

Radiation curable adhesives have enjoyed relatively rapid growth over the past years. Although they form only a small fraction of the worldwide multi-billion dollar adhesive market, they are well established in both the industrial and consumer markets (Pappas & Woods, 1990: 147-159).

Radiation curing adhesives use a photoinitiator (PI) to absorb radiation and convert into free radicals, radical ions and/or long-lived intermediates, such as acids or bases, a process that then initiates the polymerisation of functional oligomers and monomers into a cross-linked polymer network. Radiation curing is known to be one of the fastest ways of curing an adhesive (Pappas & Woods, 1990: 147-159).

Radiation curing adhesives span a whole range of different adhesive applications such as (Pappas & Woods, 1990: 147-159):

- laminating and structural assemblies
- surface mounting
- tacking and fixturing sealing
- potting and encapsulating compositions
- pressure-sensitive and hot-melt adhesives
- conducting adhesives
- conformal coatings.

The radiation curing adhesives offer several attractive features and limitations, as listed in Table 1.

Table 1: Attractive features and limitations of radiation curing adhesives

Attractive Features						
Rapid Polymer Network Formation		High Processing Speed and Productivity				
Low Heat Generation		Heat Sensitive Substrates				
One-Pack Composition		Automatic Dispensing				
Economical Ecological		Low Energy and Space Requirement Low Capital Cost Low Organic Emissions				
Limitations						
Pigmentation Fillers	=	Opacity and Rheology				
Cure Thickness =		Limited by Photoinitiator Concentration				
Geometry =		"Shadow Areas" Opaque Substrates				
Glass Transition = Temperature (Tg)		Limited by Ambient Cure				
Exterior Durability	=	Light Stabilizers tend to Reduce UV Cure Rate				

(From Pappas & Woods, 1990: 147-159)

The PI concentration in radiation curing adhesives is very important. Because most PIs are opaque, light penetration through the adhesive is a problem. Therefore the following limitation arises:

 To increase adhesive film thickness the PI concentration must decrease in order to achieve sufficient light penetration for thorough cure. However, a decrease in PI concentration means that less light is absorbed per unit volume, resulting in a slower curing rate.

It is therefore important to have the optimum PI concentration for the specific adhesive application (Pappas & Woods, 1990: 147-159).

One or more of the limitations listed in Table 1 can be overcome by having an auxiliary curing mechanism added to the radiation curing adhesive (Pappas & Woods, 1990: 147-159). Loctite® have recently developed such a product, Loctite 4307, a medium-viscosity CA adhesive using UV light as an auxiliary curing mechanism to

cure the thicker adhesive sections, giving the adhesive gap-filling properties. Gap filling is a property that conventional CA adhesive lacks (see Figure 4).



Figure 4: Gap-filling properties of photoinitiated CA adhesives

In this investigation, the PI (dibenzoylferrocene) was added to the cyanoacrylate adhesive (Loctite 454) to give the adhesive an auxiliary light curing mechanism. This auxiliary mechanism gives the adhesive gap-filling properties on rough and uneven underwater surfaces, increasing the bond strength (see Figure 4). The photoinitiator used in this investigation (dibenzoylferrocene) will be discussed next.

2.3 Photoinitiators

Conspicuously absent from most literature on photoinitiators are those that undergo the photochemical release of an anionic initiating species. Kutal *et al.* (1991) were the first to report on an attractive strategy for photoinitiating anionic polymerisation using a coordination complex.

They exploited the photochemical reaction that takes place on the irradiation of a transition metal complex. These complexes generally undergo ligand-substitution reactions, after which their ligand field absorption bands (wavelengths) overlap those of the radiation source. They suggested trans-[Cr(NH₃)₂(NCS)₄]⁻ (Reineckate anion) as the ideal anion source. The photochemical release of a thiocyanate (NCS) anion to a vinyl carbon atom of a monomer such as ethyl α -cyanoacrylate proved an effective initiator for the anionic polymerisation of cyanoacrylates (Kutal *et al.*, 1991).



The original discovery by Kutal *et al.* in 1991 drew the attention of many scientists and led to new discoveries in this field. In 1995 Palmer *et al.* (1995) suggested a new anionic photoinitiator, $Pt(acac)_2$ (structure shown in Figure 5; acac- is the anion of acetylacetone).



Figure 5: Chemical structure for Pt(acac)₂ (From Palmer *et al.*, 1995)

The photochemically produced acetylacetonate anion is also reported to be a highly effective photoinitiator for the anionic polymerisation of cyanoacrylates.

Paul *et al.* (1997) reported an anionic photoinitiator comprising Group VI metal carbonyl pyridine complexes. Arsu *et al.* (1996) reported on the zwitterionic polymerisation of alkyl cyanoacrylates by pyridium salts and on the later use of phosphonium salts.

Then in 1998 Yamaguchi *et al.* suggested ferrocene and derivatives as a new class of anionic photoinitiator. Thereafter, Kutal and others extensively investigated the characteristics of group 8 metallocenes, especially these of ferrocene and ruthenocene complexes.

We will now take a closer look at dibenzoylferrocene, the photoinitiator used in this investigation.

Dibenzoylferrocene (DFc) is an organometallic complex with a unique sandwich molecular structure. This transition metal complex is a derivative of the well-known ferrocene (Fc) $[Fe(\eta^5-C_5H_5)_2]$ complex that has been the subject of numerous

photochemical investigations (Yamaguchi *et al.*, 2007). See Figure 6 for the chemical structures of ferrocene and dibenzoylferrocene.



Figure 6: Structures of (i) ferrocene and (ii) dibenzoylferrocene

In general, the overall mechanism of photoinitiated polymerisation for a metal complex can be split into two essential steps. First, the photoinitiator (PI) complex absorbs light (photons) and then it undergoes photochemical reactions to form their electronically excited states (IN) (equation 1).

$$\mathbf{PI} \xrightarrow{\mathbf{hv}} \mathbf{IN}$$
[1]

It was found that for ferrocene and its derivatives the electronically excited state (IN) is an anionic species when irradiated in solutions containing an alkyl 2-cyanoacrylate monomer. The structures, electronic distributions and reactivities of excited states (IN) can differ substantially from the corresponding properties of the ground state.

In a subsequent thermal step, which can be recorded by calorimetric methods, the high-energy anionic initiating species (IN) reacts with the monomer (cyanoacrylate) to initiate polymer formation (polycyanoacrylate) (see equation 2).

IN + monomer \rightarrow polymer

parentage.



Yamaguchi *et al.* (2007) found that this photochemical process can occur by two distinctive pathways that originate in electronically excited states of different orbital

The excited states of transition metals will now be considered.

2.3.1 Excited states

Transition metal complexes are classified in terms of their dominant molecular orbital configuration. The transition between these electronic states can be labelled depending on the specific orbitals that undergo a change in their electron occupancy. The different transition types can be illustrated by a qualitative orbital energy diagram (Figure 7) which shows the molecular orbital obtained from mixing the valence orbitals of a transition metal, with the symmetry adapted orbitals of six ligands situated at the vertices of an octahedron.





(From Pappas, 1992: 26)

The transition types are (see Figure 7):

- ligand field (1)
- ligand-to-metal charge transfer (2 and 3)
- metal-to-ligand charge transfer (4).

For clarity, all orbitals of a given class (σ_L , $d\pi$, etc.) are represented by a single energy level (Pappas, 1992: 26).

Assuming a weak metal-ligand covalency, the molecular orbitals σ_L , π_L and π_L^* are localised mainly on the ligands, whereas $d\pi$, $d\sigma^*$, $s\sigma^*$ and $p\sigma^*$ are largely metal in character (with * denoting antibonding character and d, s and p the specific metal orbital involved).

The charge transfer excited states will now be discussed in more detail because these are said to be the main occurrences in the dibenzoylferrocene complex.

2.3.2 Charge transfer excited states

Charge transfer excited states in complexes arise from the redistribution of electron density between metal orbitals (iron, Fe) and those of the ligands (cyclopentadienyl groups) or surrounding solvent (the solvent in this case is cyanoacrylate monomer). The transition from the ligand-based electrons in the π_L orbital to a metal d orbital ($\pi_L \rightarrow d\sigma^*$, see Figure 7, number 3) produces a ligand-to-metal charge transfer (LMCT) excited state.

The opposite transition can also take place when electrons from the metal d orbital transfer to the ligand orbital ($d\sigma^* \rightarrow \pi_L^*$, see Figure 7, number 4), producing a metal-to-ligand charge transfer (MLCT) excited state.

The complex is then surrounded by a solvent. A transition that results in the movement of electrons from the complex to the solvent can occur, giving rise to a charge-transfer-to-solvent (CTTS) excited state.



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All of the transitions (LMCT, MLCT and CTTS) cause a radical redistribution of electron density in the metal, ligand and solvent involved, thereby changing the oxidation states of these species, which in turn makes then susceptible to oxidation-reduction reactions.

In certain systems $(Co(NH_3)_6^{3+}$ change to $Co(NH_3)_6^{2+})$ ligand substitution pathways become important. Where charge transfer creates an unstable metal centre, $Co(NH_3)_6^{2+}$ undergoes virtually instantaneous aquation of its ligands to produce $Co(H_2O)_6^{2+}$ in acidic aqueous solutions.

Likewise, ligands can enhance their reactivity toward processes such as protonation and electrophilic attack through changes in their charge distribution.

2.3.3 Dibenzoylferrocene

Dibenzoylferrocene is a derivative of the well-known ferrocene (Fc), a metal complex with a unique structure consisting of an iron (Fe) atom sandwiched between two cyclopentadienyl groups. Attached to each cyclopentadienyl group is an electron-withdrawing benzoyl group (see Figure 6). The addition of one or two benzoyl groups to a ferrocene molecule has a significant effect on its electronic properties, which is evident from the electronic absorption spectra for ferrocene, monobenzoylferrocene (BFc) and dibenzoylferrocene (DFc) (see Figure 8).





Figure 8: Electronic absorption spectra of Fc, BFc, and DFc

(From Yamaguchi et al., 2007)

The ferrocene complex shown in Figure 8 has weak ligand field bands. However, the benzoyl-substituted derivatives showed absorption bands with significantly higher intensities and at longer wavelengths (Yamaguchi *et al.*, 2007).

Irradiation of an air-saturated methanol solution of dibenzoylferrocene with 546 nm light causes a decrease in the longer wavelength band 1 and a steady increase in band 2 in the ultraviolet region. This gives rise to the isosbestic point at 372 nm, indicating that secondary photolysis of photoproduct(s) does not occur during the course of irradiation (see Figure 9).

(From Yamaguchi & Kutal, 2000)

Yamaguchi *et al.* (2007) found that the mixing of appreciable metal-to-ligand charge transfer (MLCT) characteristics into their respective low-energy electronic excited states is responsible for these spectral characteristics of benzoyl-substituted ferrocenes.

The limiting resonance structure depicted in Figure 10 represents the contribution of MLCT characteristics to dibenzoylferrocene, where the formal charges on iron and oxygen signify the vectorial displacement of electron density from the metal to the ligand (Yamaguchi *et al.*, 2007).

Figure 10: Resonance structure of electronically excited DFc

(From Yamaguchi and Kutal, 2000)

Conjugation between the π orbitals of the cyclopentadienyl phenyl rings and the adjacent carbonyl group allows the transferred charge to be delocalised over several atoms of the ligand, thus stabilising the MLCT excited state relative to the ground state and also lowering the transition energy.

Further evidence that the low-energy electronic absorption bands of benzoyl-substituted ferrocenes have MLCT characteristics is provided by Raman spectroscopy and can be found in the paper by Yamaguchi *et al.* (2007).

The photochemical behaviour of ferrocene is also altered by the placement of a benzoyl group onto the cyclopentadienyl rings of both monobenzoylferrocene, dibenzoylferrocene and other derivatives (see Table 2).

Compound	Solvent	<u>λ_{max} (nm),</u>	ε (M ⁻¹ cm ⁻¹)
Compound	Convent	Band 1	Band 2
Fc	Methanol	442 (91.5)	325 (51.3)
Fc	Isooctane	440 (95)	326 (55)
BFc	Methanol	483 (903)	363 (1360)
BFc	Acetonitrile	472 (780)	358 (1340)
BFc	Isooctane	459 (610)	355 (1220)
BFc-3 Me	Methanol	483 (783)	355 (1360)
BFc-CI	Methanol	483 (885)	358 (1340)
DFc	Methanol	486 (943)	353 (2090)
DFc	Acetonitrile	480 (885)	353 (2240)
DFc	Cyclohexane	469 (713)	352 (2020)
DFc	Isooctane	470 (700)	354 (1970)
DFc-o-Me	Methanol	483 (898)	346 (2080)
DFc- <i>m</i> -Me	Methanol	486 (945)	353 (2100)
DFc-3 Me	Methanol	486 (852)	345 (2160)
DFc-CI	Methanol	486 (915)	347 (2170)
DFc-CI	Cyclohexane	473 (672)	346 (1900)
DFc-F	Methanol	484 (963)	349 (2180)

Table 2: Electronic absorption spectral data for ferrocene compounds

(Data from Yamaguchi et al. 2007)

It becomes apparent that monobenzoylferrocene and dibenzoylferrocene undergo reasonably efficient heterolytic metal-ring bond cleavage in non-halogenated solvents such as cyclohexane, acetone and methanol, while ferrocene is photoinert in methanol. The quantum efficiency for mono benzoylferrocene and dibenzoylferrocene is shown in Table 3.
Run	Compound	Wavelength	Solvent	(¢ _{dis})
1	BFc	546 nm	Methanol	0.083
2	BFc-CI	546 nm	Methanol	0.098
3	DFc	546 nm	Methanol	0.42 ± 0.06
4	DFc	488 nm	Methanol	0.37 ± 0.02
5	DFc	406 nm	Methanol	0.36 ± 0.01
6	DFc	488 nm	Cyclohexane	< 10 ⁻⁴
7	DFc-o-Me	546nm	Methanol	0.41 ± 0.02
8	DFc-m-Me	546 nm	Methanol	0.41 ± 0.02
9	DFc-3Me	546 nm	Methanol	0.34 ± 0.00
10	DFc-CI	546 nm	Methanol	0.41 ± 0.01
11	DFc-F	546 nm	Methanol	0.47 ± 0.02

Table 3: Disappearance quantum yield (ϕ_{dis}) data

Note: A temperature of 22 ± 2 °C and deoxygenation by bubbling with argon did not change ϕ_{dis} .

(From Yamaguchi et al., 2007)

The photochemical reaction of dibenzoylferrocene in these solvents when irradiated with visible light can be followed in Schematic 1.



Schematic 1 (From Yamaguchi & Kutal, 2000)

Having considered in some detail the photochemical characteristics of ferrocene, in particular that of dibenzoylferrocene, the question now arises: how does dibenzoylferrocene photopolymerise cyanoacrylates and what exactly is this IN (primary initiating species) mentioned in equations 1 and 2?



The photopolymerisation of cyanoacrylate adhesives containing dibenzoylferrocene will be investigated, but first the general polymerisation mechanism for cyanoacrylate adhesives must be examined.

2.4 Polymerisation Mechanism for Cyanoacrylates

Polymerisation of cyanoacrylates via an anionic mechanism is initiated by a nucleophilic species (Nu⁻) attacking the electron-deficient carbon atom in the CH₂=C moiety (Edwards & Day, 2004). The unusual electronic environment created by the highly electronegative ester (-COOC₂H₅) and cyanide (-CN) groups allows the initiation by a nucleophilic species (Nu⁻), such as hydroxide ions (OH⁻), from the minute amount of moisture normally present on all surfaces. Other groups with initiating properties include alcohols, nitrile ions, amines, carboxylate ions and many others. The strong electron-withdrawing cyanide and ester groups keep the stability to the newly formed anion and a propagation reaction involving the addition of further monomer molecules to the anion occurs rapidly. The rapid addition of monomers causes a highly exothermic reaction (Comyn, 1998).



Figure 11: Anionic polymerisation mechanism for ethyl-2-cyanoacrylate (From Edwards & Day, 2004)



The propagation reaction (and heat generation) continues until all the monomer is consumed or until a termination species (YZ) is reached. The termination species is usually an acid, in which Y is a proton, as shown in Figure 11.

Altering the monomer will disrupt its highly reactive electron configuration and alter the adhesive properties. Structural variations are usually made only to the alkyl group within the ester. Common alkyl groups are methyl, ethyl, butyl and octyl, all having different adhesion properties.

Cyanoacrylate adhesives may contain several additives such as viscosity modifiers, plasticisers, accelerators, adhesion promoters, tougheners, cross-linking agents, fillers, dyes and colorants.

2.5 **Photopolymerisation of Cyanoacrylates**

During photopolymerisation, the anionic species required for the polymerisation mechanism described above is brought about by the irradiation of a light-sensitive chemical species (photoinitiator, PI).

Dibenzoylferrocene dissolves readily in neat cyanoacrylate to yield a solution that does not show a visual change in its viscosity when stored in a dark room for 2 weeks (see t_{therm} in Table 4). However, on exposure to light the solution polymerises first into a viscous syrup and eventually becomes a hard polymer (Yamaguchi and Kutal, 2000).

Yamagushi and Kutal (2000) measured the photoinitiating process by measuring the irradiation time required for a magnetic stirrer bar (8 mm) to cease spinning in a 1 cm rectangular transparent methacrylate plastic cuvette containing 2 ml of solution. The time required for the solution to change into a viscous syrup was recorded as t_{photo} and is shown in Table 4.

PI	PI Concentration		λ_{excit}	t _{photo}	t _{therm}
	mol/L x 10 ³	(ppm)	nm ^a	s ^b	days ^c
BFc	1.46	(404)	>290	180	32
BFc	1.90	(523)	436 ^e	>900	f
DFc	1.06	(399)	>290	3.8	16
DFc	1.61	(605)	436 ^e	38	d
DFc	2.39	(900)	546 ^f	27	d
None					>180

Table 4: Photoinitiator and thermal stability data for BFc and DFc

(From Yamaguchi & Kutal, 2000)

^a Excitation wavelength

^b Irradiation time required for sample to become so viscous that the 8 mm stirring bar ceased to spin. Samples were photolysed on the day of preparation.

^c Time required for a visually noticeable change to occur in the viscosity of a sample stored in a dark at room temperature.

- ^d Not determined
- ^e light intensity = 7.8 x 10⁻⁸ Einstein/s

^f light intensity = 1.0×10^{-7} Einstein/s

Data from Table 4 show more rapid polymerisation for solutions containing dibenzoylferrocene (DFc) than those containing monobenzoylferrocene (BFc), both with polychromatic (>290 nm) excitation, and for samples irradiated at 436 nm. Rapid polymerisation even occurs when low-energy green light (546 nm) is used, indicating that these complexes allow a wide latitude in the selection of excitation sources (Yamaguchi & Kutal, 2000).

Commercially produced cyanoacrylate monomers must be stabilised against anionic and free radical polymerisation due to ready initiation by bases and free radicals. Reported anionic inhibitors include:

- meta-phosphoric acid
- phosphorus pentoxide
- antimony oxide

- picric acid
- iron(III)chloride
- nitric oxide
- hydrogen fluoride
- sulphur dioxide
- methanesulphonic acid (MSA)
- and many other chemical species.

Free radial inhibitors/scavengers include hydroquinone (HQ), catchol and derivatives of these materials (Skeist, 1976: 570).

By adding MSA and HQ – an anionic and free radical inhibitor/scavenger respectively – to the photoinitiator/cyanoacrylate solution, valuable information concerning the nature of the primary initiating species (IN, equations 1 and 2) was learnt. It was observed that an increase in MSA (a strong proton donor) causes a dramatic increase in t_{photo} for both complexes, as shown in Table 5.

These data agree with those obtained by Sanderson *et al.* (2002) who used attenuated total reflectance infrared spectroscopy (ATR-IR) to follow the degree and rate of polymerisation directly over time. The commercial cyanoacrylate monomer has 5-10 ppm of MSA scavenging for traces of basic impurities and exhibits a short induction period before rapid polymerisation, which finally approaches a plateau at 80-90% conversion (see Figure 12).



Figure 12: Effect of MSA on anionic photopolymerisation

(From Sanderson et al., 2002)

Increasing the acid concentration clearly demonstrates that sufficient anionic species (increased induction) are required to neutralise this increased acid content before polymerisation occurs (see 150 ppm MSA added, Figure 12).

Photoinitiator (PI)	Concer	t _{photo}		
	PI	MSA ^a	HQ⁵	5
BFc	2.36	0.050	9.5	200
BFc	2.36	5.1	9.5	>600
BFc	2.36	0.050	29	220
DFc	1.07	0.050	9.5	3.8
DFc	1.06	1.6	9.5	37
DFc	1.14	6.0	9.5	>600
DFc	1.07	0.050	29	3.6

Table 5: Effect of scavengers on photopolymerisation of cyanoacrylate

^a MSA – methanesulphonic acid (base scavenger); ^b HQ – hydroquinone (radical scavenger)

^c Samples were irradiated with the Pyrex-filtered output of a 200 W high-pressure mercury-arc lamp. (From Yamaguchi & Kutal, 2000).



However, large increasing the concentration of HQ does not significantly affect t_{photo} for both BFc and DFc (see Table 5, t_{photo} increase for BFc but decreased for DFc). It was also observed that the oxygen content of the sample does not affect t_{photo} (quantum yield, Table 3). Data compiled from Table 5 therefore suggest that the primary initiating species (IN) is not a radical, but is instead a Bronsted base which initiates the anionic polymerisation of cyanoacrylate (Yamaguchi & Kutal, 2000).

The possibility that IN is a cyanoacrylate radical anion was also investigated. It is known that ferrocene forms a photoactive ground-state complex with an electron-accepting solvent such as CCI_4 – this is a characteristic of charge-transfer-to-solvent (CTTS) excitation. Irradiation therefore causes a one-electron oxidation of ferrocene to the ferricenium cation and reduction of the solvent to its radical. Cyanoacrylate solution containing DFc, however, shows no evidence for a CTTS band in the electronic absorption spectrum. Cyanoacrylate radical anions can therefore be discounted as the IN (Yamaguchi & Kutal, 2000).

Irradiation of BFc and DFc releases benzoyl-substituted cyclopentadienide ions (see Schematic 1 in Section 2.3). These carbanions are strong Bronsted bases and could be playing the role of the IN (equations 1 and 2). This theory was tested by independently synthesising a sodium salt, $Na^+[C_5H_4C(O)C_6H_5]^-$, of the benzoyl-substituted cyclopentadienide ion and adding it to a cyanoacrylate monomer. A droplet of this independent carbanion caused a rapid polymerisation reaction, accompanied by the evolution of heat. This rapid reaction is suggest that the benzoyl-substituted cyclopentadienide ions generated during irradiation of a BFc and DFc (and derivatives of DFc) are responsible for the rapid initiation of cyanoacrylate polymerisation (Yamaguchi & Kutal, 2000).

Designating this carbanion as the IN can be further proven by comparing the data from the disappearance quantum yield (ϕ_{dis} , Table 3) with the polymerisation time (t_{photo} , Table 4). The higher the disappearance quantum yield is, the higher the carbanion formation, resulting in a shorter polymerisation time. This comparison shows that dibenzoylferrocene is a more effective photoinitiator than

monobenzoylferrocene because of the more effective formation of carbanions (Yamaguchi & Kutal, 2000).

It can therefore be concluded that it is the benzoyl-substituted cyclopentadienide ion (see Figure 13) formed during the proper irradiation of DFc (see Schematic 1 in Section 2.3) that plays the role of the primary initiating species (IN) in solutions containing cyanoacrylate monomer.



Figure 13: Benzoyl-substituted cyclopentadienide ion

(From Yamaguchi & Kutal, 2000, see Schematic 1 above)

An ethyl cyanoacrylate adhesive gel was therefore chosen for our underwater application initiated with DFc. DFc showed several advantages above other ferrocenes, namely higher absorption and quantum yield (488 nm) close to 470 nm blue LED light, short polymerisation time (t_{photo}) and good thermal stability. Since DFc is readily available from commercial suppliers, further synthesis for ferrocene was not necessary.

2.6 Adhesive Joints

In this section the effect of water (moisture) on adhesive joints is discussed. A short explanation using the Dupré equation is used to show that water has the ability to displace organic adhesive from metal surfaces and is probably the main failure mechanism of cyanoacrylates on metal surfaces. Finally, anodising metal surfaces are discussed as a method of improving adhesion to underwater metal surfaces.

2.6.1 Effect of water on joint strength

Both water and moist air cause the greatest reduction in bond strength when an adhesive is exposed to these environmental conditions (Comyn, 1983: 86). Waite (1987) puts it more simply: "Water and adhesives are in conflict".

Comyn (1983) studied the kinetics and mechanism of environmental attack and reported on many studies in the literature that have demonstrated the nature of bond failure in natural and laboratory climates.

The mechanism by which water alters the adhesive bond strength can be by one or a combination of the following processes (see Figure 14). Firstly, water may enter the joint by:

- 1. diffusion through the adhesive polymer itself
- 2. diffusion through the substrate if it is permeable
- 3. wicking, i.e. the transport of water along the interface between the substrate or filler material
- 4. capillary action into small cracks and crazes (more likely in aged bonds).

Secondly, once the water has already entered the joint, it may cause weakening by one or a combination of following:

- 5. affecting the properties of the adhesive in a reversible manner such as plasticisation
- 6. affecting the properties of the adhesive in an irreversible manner such as hydrolysing, resulting in cracking or crazing
- attacking the adhesive/substrate interface either by displacing the adhesive or hydrating the metal or metal oxide surface of the substrate
- 8. inducing swelling stresses in the adhesive joints.





Figure 14: Mechanism of water attack on adhesive joints

(Reproduced and modified from Waite, 1987)

The importance of the displacement mechanism noted in point 7 above can be illustrated by the following Dupré equation. The work needed to separate two phases of unit area that are in contact in dry air is related to the surface free energy by:

$$\mathbf{W}_{A} = \mathbf{\gamma}_{x} + \mathbf{\gamma}_{y} - \mathbf{\gamma}_{xy}$$
[3]

Similarly, in liquid surroundings, the work of adhesion is:

$$\mathbf{W}_{\mathsf{L}} = \gamma_{\mathsf{x}\mathsf{L}} + \gamma_{\mathsf{y}\mathsf{L}} - \gamma_{\mathsf{x}\mathsf{y}} \tag{4}$$

where

$$\begin{split} W_A \text{ and } W_L &= \text{the work of adhesion in air and liquid surroundings respectively} \\ \gamma &= \text{the surface free energy, with the respective space co-ordinates, x & y,} \\ &\text{and xL & yL in liquids.} \end{split}$$

Large positive values of W_A indicate thermodynamic stability, like those for adhesivemetal(oxide) bonding in air, but in water W_L is negative, indicating instability. Therefore water has the ability to displace organic adhesives from metal-oxide surfaces (Kinlock, 1981: 282).



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2.6.2 Effect of moisture on the strength of cyanoacrylate bonds

Drain *et al.* (1985) found that ethyl cyanoacrylate bonds between polycarbonate substrates are extremely water resistant compared with steel-steel bonds (see Figure 15). The cured cyanoacrylate itself has been shown to be relatively impermeable to water and due to the fact that ethyl cyanoacrylate dissolves the polycarbonate surface layer, no real adhesive/substrate interface is formed. As no interface is present, the water cannot enter into the bond to damage the bond by the mechanisms mentioned above (points 5 to 8).

The resultant adhesive material is therefore a blend of polycarbonate and polyethyl cyanoacrylate.



Figure 15: Effect of humidity ageing on cyanoacrylate adhesive (From Drain *et al.*, 1985)

It is believed that steel-steel bonds quickly lose their bond strength due to the water vapour diffusing through the metal oxide/adhesive interface. The water reacts with

bonding surface (see the Dupré equation above).



the oxide layer and forms ferric oxide, and it can also displace the adhesive from the

It is possible that the corrosion products and water may even cause hydrolytic degradation of the adhesive at the interface and gradually damage the bond to the centre of the assembly (Drain *et al.*, 1984).

Adding small concentrations of acetic acid to ethyl cyanoacrylate adhesives has been proved to promote adhesion to metals. Selectivity towards the type of metal has been shown with regard to steel, stainless steel and duraluminium. It is believed that acetic acid molecules help displace the absorbed water molecules from the oxide surface, making it possible for the polar adhesive groups to bond to the oxide directly or through an acetic acid intermediate (Kotzev *et al.*, 1987).

Cyanoacrylate adhesive can be further modified to improve tensile shear strength and deformation stress relaxation of bonds by introducing polymers with high molecular weight. Polymethyl methacrylate (PMMA)-modified adhesive is reported to improve joints bearing static loads, while joints bearing cyclic or vibrating loads can be improved by adding polybutadiene-co-acrylonitrile (PBAN) to cyanoacrylate adhesives (Petrov et al., 1988).

It should be kept in mind that although the effect of moisture on joints has been extensively studied (dry joints exposed to moisture), there are few studies available in the literature on bonds made underwater and then aged. In the latter case, water is already present on the bond line and probably in the adhesive itself.

2.6.3 Anodising metal surfaces

The purpose of the adhesive (Category 1) developed in this study is to form underwater bonds in a very short time. There is, however, very little that can be done to improve adhesion to untreated surfaces already underwater in the short period before adhesion takes place. If it is known that a metal surface requires to be bonded underwater, it is recommended that the metal be pre-treated by etching or anodising the surface. This will not only improve adhesion, but also reduce corrosion (Armstrong, 1997).

Anodising produces a porous oxide film on the metal surface and has a number of advantages over other pre-treatment methods, these being (Armstrong, 1997):

- The porous oxide film provides for mechanical interlocking and the size of the pores is dependent on the anodising method used.
- The oxide film is not electrically conductive, thereby reducing corrosion by preventing the flow of electrons.
- Chemical bonding of the adhesive to the oxide layer is possible.

The anodised film consists of a close-packed hexagonal array of oxide cells; the cells each have a cylindrical pore from the top surface all the way to the base of the metal (see Figure 16).



Figure 16: Drawing of anodised film on aluminium (phosphoric acid) (From Venables *et al.*, 1979)

The structural dimensions of the oxide film depend on the anodising conditions and the acid (electrolyte) used. Sulphuric acid forms smaller pores compared to those of phosphoric acid and these have diameters of 20 nm and 45 nm respectively (Mittal, 1983: 32).

Popular acids for etching and anodising metal surfaces include:

- sulphuric acid
- chromic acid
- phosphoric acid

of which phosphoric acid generally gives superior joint durability (see Figure 17).





(a) degreased;
(b) sulphuric acid anodised;
(c) chromic acid etched;
(d) chromic acid anodised (e) phosphoric acid anodised
(From Kinloch, 1981: 235)

On aluminium, chromic acid and phosphoric acid are widely used to improve bond durability. Sulphuric acid anodising gives poor bonding durability but is excellent for corrosion protection. The poor bonding to aluminium anodised with sulphuric acid is a



result of failure between the metal and metal oxide layer, or failure within the oxide layer itself (Kinloch 1981: 233).

Pre-treatment of metals is therefore essential for obtaining strong underwater bonds. Degreasing or the mechanical treatment of metal surfaces, such as grit blasting, are in most cases inadequate and show poor durability in water. However, exceptions have been noted. If joints are to be subjected to humid conditions, it is advised to use an etching or anodising pre-treatment (Kinloch 1981: 233).

2.7 Photo-curing Analysis

Calorimetric analysis can be a useful tool in the formulation of a light-curing adhesive. No matter what the final application, calorimetric analysis can help determine the rate, degree of cure and ultimately the kinetics of the photopolymerisation material (Pappas, 1992: 57).

In order to obtain the full kinetics, one should utilise complementary techniques, such as thermal, spectroscopic and mechanical analyses. Spectroscopic techniques have been used in the past to determine the kinetics for similar anionic polymerisation of cyanoacrylates, but there is little thermal analysis data available using a photo differential scanning calorimetry (photo-DSC technique). The author therefore decided to use thermal data from photo-DSC to aid formulation, as well as data on shear bond strength.

The anionic polymerisation of cyanoacrylate adhesive has been studied by various other researchers such as Yang (1993) who used real-time Fourier transform infrared spectroscopy (FT-IR) to study the kinetics of the transition metal complex of trans-Cr- $(NH_3)_2(NCS)_4^-K^+$ as a photoinitiator. Kutal also reported on the use of real-time FT-IR to study the anionic polymerisation of cyanoacrylates using ferrocene derivatives similar to the photoinitiator used in this investigation (Kutal, 1997 and Kutal & Yamaguchi, 2000).

2.7.1 Photo differential scanning calorimetry

The differential scanning calorimeter (DSC) is the most widely used exotherm apparatus. It can be modified to allow light penetration into the sample chamber. The Perkin Elmer DSC-7 apparatus can be easily modified by machining holes above the sample and reference cells into the DSC-7 sample cell cover. The holes are sealed with a quartz window to provide a small chamber which can be purged with inert gases before and during testing. The light source is directed to fall on both the sample and reference cells, and is usually fitted with a shutter to control the illumination time (Pappas, 1992: 67).

It is necessary for the adhesive to produce a detectable amount of heat during the curing process for it to be accurately followed by calorimetric technique. No matter what the mode of polymerisation is (free-radical, cationic or anionic), the total heat evolution is the consequence of the sum of the heat produced during initiation, propagation and termination. This process is best described by the reaction sequence.

Light absorption and bond cleavage

PI
$$\xrightarrow{hv}$$
 Nu⁻ (little to no heat generated)

[5]

Initiation



[6]



Propagation



Termination



[8]

The total heat measured is therefore the sum combination of all the initiation, propagation and termination processes per mass unit sample. The propagation step can be broken into an endothermic breaking of a carbon-carbon double bond and the formation of two carbon-carbon single bonds in an exothermic process. The amount of heat generated is therefore the difference between the endothermic breaking (single C=C) and the exothermic bonding (two C-C) process (Pappas, 1992: 60).

2.7.2 Exotherm curves

(Pappas, 1992: 70 - 73)

The photopolymerisation of a sample at a constant temperature (isothermal) generates heat from the sample; the rate of heat evolution (mcal/s) is recorded over time, and the curve obtained is known as an 'exotherm' (see Figure 18). The percentage conversion can be calculated from this curve, at any selected time, from the integrated area under the rate-versus-time curve from the initiation point to the selected time, divided by the total integrated area. The total area is the point in time where 100% conversion is expected.





Figure 18: Typical exotherm of photopolymerisation (isothermal) (From Pappas, 1992: 70)

An induction period (t_{ind}) can be seen in many photopolymerisation exotherms. This is a stable period from the opening of the light shutter to the onset of polymerisation. Induction can be the result of several factors, all of which inhibit the onset of polymerisation. The rate of heat evolution then accelerates dramatically to the point where the maximum or fastest rate of polymerisation is attained (H_{max}) at a given time (t_{max}). Thereafter the amount of monomer available for reaction decreases and the amount of heat generated is reduced. As the viscosity increases, the mobility of the chains decreases, making bonding more difficult, up to the point where no more heat evolution can be detected by the instrument and the exotherm curve has returned to its baseline.





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It is convenient to define the time to attain 95% conversion as t_{95} . This is used because the end point where the exotherm curve returns to the baseline to obtain 100% conversion is not always easy to define.

The ultimate percentage conversion is one of the most useful pieces of information that can be obtained from the exotherm. The total integrated area under the exotherm is compared with the expected enthalpy of polymerisation corresponding to the size of the sample. If the integrated exotherm curve from the time t_{zero} (first exposure to light) to time (t') is compared with the total heat at 100% conversion, than the measured peak height at H' (see Figure 18) is the percentage conversion at time (t').

The rate constant, k, can also be deduced from the exotherm at any time (t') using the following equation (Pappas, 1992: 72):

$$\mathbf{k} = \mathbf{H'} / [\mathbf{M}]' = \mathbf{H'} / \Delta \mathbf{H} - \mathbf{AREA'}$$
[9]

where

H'	=	peak height at time (t')
$[M]' = \Delta H - AREA$	=	monomer concentration in terms of heat (kcal/mol) remaining
		at time (t')
ΔH	=	total heat expected from sample if all monomer units are
		converted
AREA'	=	integrated area under exotherm curve from time zero to time
		(t')

An autocatalytic kinetic model can be used to do kinetic analysis of a typical photopolymerisation exotherm, where α is the fraction of monomer converted to polymer at a given exposure time (see equation 10).



$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \mathrm{k}\,\alpha^{\mathrm{m}}\,\left(1-\alpha\right)^{\mathrm{n}}$$

where

- $d\alpha/dt$ = polymerisation rate
- k = composite rate constant
- m = order of dependence on converted fraction α
- n = order of dependence on unconverted fraction 1- α

[10]

CHAPTER 3: EXPERIMENTAL

This chapter gives the experimental details with regard to the materials, instrumentation and methods used during this investigation.

3.1 Materials

The chemicals used in this investigation are discussed below. The different types of substrate materials used during the testing for bond strength are discussed in Section 3.5.

3.1.1 Monomers, photoinitiators and other materials

The ethyl cyanoacrylate gel (Loctite 454, 20 g tubes) was purchased from a Loctite supplier and used without modification (see Appendix D for Loctite 454 data sheet). Not all cyanoacrylate adhesives react with dibenzoylferrocene in the same manner as Loctite 454. A mixture of Loctite 454 or Loctite 406 and 0.2% dibenzoylferrocene is a light orange colour. On illumination with blue light, the adhesive solidifies and remains the same colour. However, other brands of cyanoacrylate, like 'Turbo Fuse' from Palm Labs, and products from Evobond (butyl and octyl cyanoacrylate), become a purple colour on irradiation and do not solidify as quickly as the Loctite brands. The reason for this is not known and was not investigated here. It is believed to be caused by different acid stabilisers used by the different manufacturers.

Dibenzoylferrocene (DFc) (an orange/red powder) was purchased from Sigma Aldrich Chemicals and used without further purification in hexane. Little toxicology information is given on the material safety data sheet (MSDS) for DFc, but the necessary safety procedures were followed when working with this chemical.

Sea water was simulated by using 'Ocean Fish', an aquarium product supplied by Prodac. All other chemicals were supplied by Sigma Aldrich Chemicals.

3.2 Light Source

The 5 mm blue ultra-bright LEDs used for the light source are manufactured by Nichia Corporation (Model: NSPB 500S) and were supplied by RS Components, South Africa. A 12 x 12 array (144 LED) light source was custom-designed using parallel connections of three LEDs and a resistor in series and sealed inside an acrylic box to allow underwater illumination of the substrates.





Forward Current vs. Dominant Wavelength



Figure 19: Typical characteristics of blue LED NSPB 500

(From Nichia Corporation)

The specifications for the Nichia blue LED can be found at the following link: http://www.nichia.com/specification/led_lamp/NSPB500S-E.pdf

The LED's dominant (peak) wavelength is influenced by the forward current and the ambient temperature, as shown in Figure 19.

The light source was powered by a Deluxe Universal Regulated DC Power Supply (Model RC-1200) by Vanson, connected to the AC mains. The output was set at 12 V DC and the current measured was 750 mA.

3.2.1 Light source calibration

The light source was calibrated by the National Metrology Institute of South Africa (NMISA) by comparing the spectral irradiance of the blue light LED array against the spectral irradiance of a standard lamp, traceable to the national measuring standard for spectral irradiance.

The measurements were taken on a grating monochromator with an integrating sphere at the entrance and a photomultiplier as the detector. The measurements were performed over the wavelength range 400 to 550 nm every 1 nm. The monochromatic bandwidth was 2 nm. The light source was positioned with the panel support plate held in a vertical position, with the centre of the unit aligned along the optical axis of the monochromator entrance optics. The distance between the centre of the LED array and the receiving aperture (with a diameter of 10 mm) of the monochromator was 1.00 m (see Figure 29, Section 4.1.1).

The 12 V DC power supply and light source were allowed to stabilise for 30 minutes before measurements were taken.

The light was calibrated at an ambient temperature of 24 $^{\circ}C \pm 2 ^{\circ}C$ and a relative humidity of 50% RH \pm 15% RH.

3.2.2 Sample illumination

The light intensity normally increases as the distance between a single LED and the light meter decreases. This is, however, not true for an LED array with a narrow angle of view (15°) and relatively large spacing between the LEDs (7.62 mm apart)



on the circuit board. This creates a minimum illumination distance of 28.94 mm, as shown in Figure 20.



Figure 20: Minimum illumination distance

The light intensity should therefore peak at a distance of just more than 28.94 mm. In this investigation the samples were illuminated at a distance of 50 mm away from the light source, this distance was arbitrary chosen to insure overlapping of the light beam (> 28.94 mm) and to fit equipment between the light source and the adhesive sample.

3.3 Ultraviolet-Visible Spectroscopy (UV-Vis)

The electronic absorption spectra of a 1.8×10^{-4} M solution of 1,1 dibenzoylferrocene (the photoinitiator) were measured in methanol at room temperature (Cary 300 Conc UV/Vis Spectrophotometer). The spectral changes were recorded at several irradiation intervals as noted in Figure 31, Section 4.1.3. The absorption spectra results correlate well with the spectra measured by Yamaguchi and Kutal (2000) (see Figure 9).





The spectral total transmittance of the polycarbonate top substrate and DSC head window (10 mm thick) was measured in the wavelength region 350 to 550 nm on a double-beam, double-dispersion spectrophotometer. The results of the measurements are traceable to the national measurement standards for transmittance. The transmittance measured by the NMISA is shown in Figure 30, Section 4.1.2.

A combination of the spectra for the light source, the polycarbonate and the photoinitiator is shown in Figure 32, Section 4.1.3 – note the different axes.

3.4 Thermal Analysis

3.4.1 Photodifferential scanning calorimetry (photo-DSC)

The isothermal photopolymerisation was performed on a Perkin-Elmer Differential Scanning Calorimeter 7 (DSC-7) with Intracooler using Pyris software. An indium standard was used to calibrate the temperature and enthalpy scales.



Figure 21: Photo-DSC set-up

The DSC head was modified with a single polycarbonate window covering both the sample and the reference cells (see Figure 21 and Figure 22).

Experimental



The polycarbonate window was replaced after several tests because blooming from the cyanoacrylate samples would affect transparency. The blue LED light source was fitted 50 mm above the measuring pans. The light was switched on and off manually using a timer without a shutter to simulate the underwater bonding procedure.



Figure 22: Photo-DSC set-up with Pyris software

Aluminium sample pans were used with depths of 0.5, 0.8, and 1.2 mm to control the sample thickness (see Figure 23).



Figure 23: Aluminium sampling pan

Nitrogen was used to purge the sample chamber before analysis. The instrument pans were cleaned by heating to 600 °C after every run. The instrument was left to regain control at every set isothermal temperature before testing. A 3-minute holding



period was used after a new sample had been placed into the instrument for the baseline to stabilise.

3.4.2 Thermogravimetric analysis

For thermogravimetric analysis a Mettler Toledo TGA/SDTA 851e Analyser was used to determine the filler content of Loctite 454. The sample was placed in a 70 μ l platinum crucible and heated from 30 to 1 100 °C at 10 °C/min. Air was passed through the sample chamber for the entire duration of the experiment (see Figure 33, Section 2.4).

Isothermal thermogravimetric analysis was done at 30° C and at 50° C to determine the rate of evaporation of Loctite 454. The sample was placed in a 70μ l platinum crucible and kept at a constant temperature for 60 minutes. Nitrogen was passed through the sample chamber for the entire duration of the experiment (see Figure 34, Section 2.4).

3.5 Substrate Materials for Tensile Testing

3.5.1 Metals

Commercial mild steel sheet (carbon, 12%, hot rolled), stainless steel 304, and aluminium were cut into blocks of dimensions $10 \times 100 \times 100$ mm (ASTM D 4501-01 – see Appendix C). The bonding surfaces of the different metal substrates were sanded with a selected grit of sandpaper (100 grit) and then cleaned with a lint-free cloth soaked in isopropyl alcohol.

The sulphuric-acid-anodised aluminium was used as supplied. Care was taken not to touch the anodised bonding surface.

3.5.2 Polymers

All polymers were supplied by Maizeys Plastic, except for the fibre-reinforced polyester (FRP) which was cast using Plastocure glass fibre and polyester resin.

Experimental

3.6 Bonding Process

The underwater bonding process of cyanoacrylate adhesives is vital to the strength of underwater bonds. The substrates were sanded with 100 grit sandpaper and thereafter cleaned with a lint-free isopropyl alcohol cloth. The top substrate was always clear polycarbonate to allow the adhesive sandwiched between the two substrates to be easily illuminated. Into the 19 mm diameter pencil ring drawn on the top substrate block, 0.5 g (\pm 0.01 g) of adhesive was placed (see Figure 24). This was done to keep constant the surface area of the adhesive exposed to water.



Figure 24: Illustration of active and inactive bond areas between substrates

The average bond line thickness is measured at 0.2 mm. The bottom substrate is left inside the water bath for 5 minutes before bonding to ensure that the substrate temperature is that of the surrounding water temperature. The top substrate is then submersed into the water bath and pressed firmly onto the bottom substrate. The adhesive is spread over the entire bond area. The light source is submersed and kept at a distance of 50 mm away from the bond line.

Immediately before bonding, the adhesive's outer surface (inside the 19 mm ring on the top substrate), which is exposed to the water, rapidly polymerises and forms a protective skin as explained in the patents by Card & West (1988a and 1988b). The cyanoacrylate adhesive that cures from the reaction with water has a white colour, whereas the cyanoacrylate cured by the radiation from the blue light source is orange. This white-coloured skin has already polymerised (polyethyl cyanoacrylate, PECA) and can therefore no longer bond the two substrates together.

The adhesive squeezed out from under the skin between the two substrates is therefore responsible for the bond strength. The inactive PECA skin trapped between the two substrates had an average diameter of 21 mm (standard deviation, 1.68 mm see Figure 25).



Figure 25: Inactive area on top substrate evident after bond failure

This inactive bond area (346 mm²) was therefore subtracted from the total bond area (2 500 mm²) to give, on average, an active bond area of 2 154 mm² for calculating the shear bond strength (see Figure 24 and Figure 25).

3.7 Tensile Testing

3.7.1 Test method (ASTM D4501 - 01)

ASTM D4501 – 01: Standard Test Method for Shear Strength of Adhesive Bonds Between Rigid Substrates by the Block-Shear Method describes a procedure and fixture used to determine the shear bond strength obtained for substrates with moduli higher than the modulus of the adhesive. A copy of ASTM D4501 – 01 is attached as Appendix C. This test method is also used by North Sea Resin (NSR) to report their commercial product's bond strength to underwater surfaces.

3.7.2 Testing apparatus

The testing instrument used for this method was an Instron 4303 by Instron Corporation with a Series IX Automated Materials Testing System 1.38. The instrument has a maximum capacity of 25 kN in tension. This is less than the required 44 kN in tension specified by ASTM D4501 - 01, but the expected bond strength underwater is lower.

The shearing fixture consists of a holding block and a shearing blade, as shown in Figure 26.





Figure 26: Illustration of the holding block and shearing blade

The shearing fixture was designed to accommodate various substrate dimensions. When thin substrate materials are tested, a slider can be inserted into the holding block and is kept in position with two wing nuts (see Figure 27). Experimental





Figure 27: Section of the holding block, slider and shearing blade

Figure 27 illustrates how the shearing blade fits around the clear top substrate and how the bottom substrate (substrate 2) is kept in position by the slider inside the holding block. A slit in the bottom of the base of the holding block prevents the shearing blade from slipping off the top substrate.



The shearing blade can accommodate top substrates up to 55 mm wide and 70 mm in height. The maximum thickness of the top substrate is 10 mm. If the substrate is any thicker, the shearing blade does not slide into the guiding slit in the base of the holding block.



Figure 28: Tensile set-up with shearing blade in position

The ASTM method requires at least five specimens for each test condition. A minimum of five tests were therefore conducted for each data point reported.

3.7.3 Test procedure

The holding block was fitted into the bottom fixed base of the Instron tensile testing machine and the shearing blade to the top cross-head clamp.

The test substrates were then placed into the holding block in such a way that the bottom substrate (substrate 2) was engaged by holding block only. The shearing blade was then slid into the slit in the holding block base, with the hole in the shearing blade engaging the top clear substrate (substrate 1) only. The cross-head was then lowered to clamp the shearing blade.

The test substrates were sheared at a rate of 1.26 mm/min. The maximum force sustained by the substrates was recorded by the Instron instrument.

CHAPTER 4: RESULTS AND DISCUSSION

This chapter presents the experimental results for the spectral measurements done on the light source and photoinitiator. The spectral information for the polycarbonate used as the photo-DSC window and for the top substrate (substrate 1) is also given. Thermogravimetric analysis (TGA) was used to determine the filler content (5%) and evaporation rate of Loctite 454. Photo-DSC results provide the optimum photoinitiator concentration and temperature kinetics. The experimental problems with the photo-DSC technique are highlighted and finally the various different bond strength determinations are reported.

4.1 Spectroscopy Results

The light source calibration and the transmittance for the polycarbonate photo-DSC window and top substrate were done by NMISA. The spectrum obtained from the photoinitiator (dibenzoylferrocene) was merely used to confirm that the unpurified dibenzoylferrocene reacted in the same way to light radiation with the custom-designed light source as that obtained by Yamaguchi and Kutal (2000) see Figure 9, Section 2.3.3.

4.1.1 Light source calibration

Figure 29 depicts the spectrum obtained from the custom-designed light source with a peak wavelength λ_p at 467 nm and an intensity maximum of 18.23 μ W/cm² at 1 m away from the light source. The centroid wavelength λ_c was calculated at 468.6 nm and the bandwidth at 50% intensity, $\Delta\lambda_{0.5}$, was measured as 24.6 nm.





Figure 29: Spectrum from blue LED (12 x 12 array) light source

The uncertainty of the calibration was 0.01 mW/cm² \pm 7%. The calibration correlates well with the data supplied by the Nichia Corporation. The small drop in the peak wavelength λ_p (470 nm for Nichia and 467 nm calibrated) could be due to higher forward current through the LEDs, as illustrated in Figure 19, Section 3.2.

The light source intensity measured at 50 mm from the light source was 6 mW/cm². The intensity drop as light passes through polycarbonate will be discussed next.

4.1.2 Polycarbonate transmittance

The transmittance of the thick polycarbonate top substrate was measured to determine the intensity loss through the polycarbonate during the bond strength determination and photo-DSC analysis.




Figure 30: Spectra for polycarbonate (thickness 10 mm)

The effective light intensity onto all the adhesive samples was taken as 5 mW/cm², 86% (transmittance of clear polycarbonate at 467 nm, see Figure 30) of the measured intensity at 50 mm away. Sanded polycarbonate top substrate was not measured as the transmittance would not be significantly altered because light scattering is reduced when the adhesive fills the scratch marks left behind from sanding making the polycarbonate-adhesive interface quite transparent.

4.1.3 Photoinitiator

The photoinitiator was supplied by Sigma Aldrich and was used without purification. Yamaguchi and Kutal (1999) purified dibenzoylferrocene by dissolving it in hexane and then recrystallising it from the solution. The question arises whether the unpurified dibenzoylferrocene would react in the same way to light from the blue (467 nm) custom-designed light source as Yamaguchi and Kutal (2000) found with their experiment using 546 nm light (see Figure 6).

The spectral changes measured at different time intervals (see Figure 31) in a 1.8 x 10^{-4} mol/l solution of 1,1-dibenzoylferrocene in methanol were measured. The solution was irradiated with the 467 nm LED light source positioned inside the

instrument at 50 mm away from the solution. The light intensity at this distance is 6 mW/cm^2 .

The spectral scans at different light exposure intervals shown in Figure 31 give an isosbestic point at 372 nm, at the same point where Yamaguchi and Kutal (2000) observed it. It is clear that to the left of the isosbestic point the solution absorbance increases and to the right it decreases.



Figure 31: Spectral changes measured for photolysis of DFc

The disappearance quantum yield (ϕ_{dis}) can be calculated for the data shown in Figure 31, but this was not done as Yamaguchi *et al.* (2007) have already calculated the disappearance quantum yield in carefully controlled experimental conditions at several wavelengths and different ferrocene derivatives (see Table 3).

The spectra shown in Figure 31 relate closely to the literature data and the dibenzoylferrocene was therefore used without further purification and was expected to react in the same manner as that found by other researchers.

All the spectra from the experiments mentioned above were overlapped on the same graph for clarification (see Figure 32, with arrows indicating the relevant axes).





Figure 32: Spectra for polycarbonate, light source and photoinitiator

It is clear from the figure that the light source intensity peak (467 nm) and the photoinitiator peak (483 nm) are relatively close (16 nm) and that the transparencies of the 10-mm-thick polycarbonate top substrate and the photo-DSC window are at their highest at 86% transmittance.

4.2 Thermal Results

The fillers used in cyanoacrylates are usually polymethyl methacrylate (PMMA) or fumed silica. A sample of Loctite 454 was dissolved in a large amount of acetone. After the solution had been standing for one day, it separated into a clear top and a white cloudy bottom layer. This bottom layer was separated and washed several times with acetone. The acetone was evaporated and a white powder remained. The powder was heated in a metal crucible to red hot with a gas torch. It did not show any discoloration and remained white. It was therefore concluded to be fumed silica filler. Powder X-ray diffraction (XRD) results could not positively identify the filler, but confirmed that the material was amorphous, strengthening the assumption that the filler was in fact fumed silica.

The amount of filler was determined quantitatively using TGA analysis.

A 36.595 mg sample was heated from 30 to 1 100 $^{\circ}$ C in air at 10 $^{\circ}$ C/min. The residue (fumed silica) had a mass of 1.813 mg and therefore the filler content amounts to about 5% on a mass basis (see Figure 33).



Figure 33: TGA temperature scan for Loctite 454

During the photo-DCS analysis, the polycarbonate window between the light source and the sample showed severe blooming (polycyanoacrylate powder) resulting from the evaporation of the cyanoacrylate monomer, especially at high temperatures.

The rate of evaporation was calculated by isothermal TGA analysis at 30 and 50 $^{\circ}$ C. A sample of about 20 mg was held isothermally for a period of 60 minutes and the mass lost over this period was recorded.



The rate of evaporation was higher at the higher temperature, with a linear dependence over the entire recording period (see Figure 34). The rate was determined to be 11 and 34 mg/m².s at 30 and 50 °C respectively. This can have a detrimental effect on the repeatability of the photo-DSC data.



Figure 34: Rate of evaporation of Loctite 454 at 30 and 50 °C

During the time from when the sample is inserted into the DCS until the instrument stabilises for analysis there may be a large variation in the true sample mass analysed, especially between high and low temperatures.

A method used by Macarie & Ilia (2005), namely placing a polyethylene terephthalate (PET) film over acrylate samples to prevent oxygen inhibition, was attempted to prevent the evaporation of the cyanoacrylate sample. However, it was found that placing a PET film over the aluminium pan filled with cyanoacrylate gel causes several problems:

 Bubbles may be trapped if the PET film is not positioned carefully over the pan.

- If there is a small gap or bubble between the gel and the film, blooming of the film will prevent light penetration.
- Heat flow from the aluminium pan to the PET film during polymerisation causes the shape of the exotherm to differ substantially.
- Placing an extra surface in contact with the cyanoacrylate gel is also undesirable as it constitutes yet another area where impurities can initiate uncontrolled polymerisation.

The photo-DCS measurements were therefore conducted without a PET film. A pure cyanoacrylate sample (no photoinitiator) was placed in the reference pan to compensate for a possible endothermic heat of evaporation in the adhesive.

4.2.1 Experimental problems with photo-DSC

Cyanoacrylates generate large amounts of heat during polymerisation. Calorimetric techniques seem ideal to follow their kinetics. Cyanoacrylates are, however, among the most reactive monomers known, and certainly the most reactive so far examined kinetically. Pepper (1978) and co-workers published several papers on the kinetics and mechanism of polymerisation of cyanoacrylates and used special experimental conditions to obtain reproducibility, but even under closely controlled conditions reproducibility remained a problem.

It is worth stressing once again the difficult experimental problems faced in following the polymerisation of cyanoacrylates using a calorimetric technique. The polymerisation of acrylate adhesives is easily followed using photo-DSC analysis, but cyanoacrylate adhesives pose several problems. The problems faced by Pepper and co-workers are discussed elsewhere (Pepper, 1980).

The problems experienced in this investigation were as follows:

- The Loctite 454 monomer is a commercial off-the-shelf product. The purity and difference in purity from batch to batch were not determined.
- The photoinitiator was used without further purification in hexane.



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- Low-intensity UV and visible light can cause a photochemical reaction in dibenzoylferrocene and initiate polymerisation of the cyanoacrylate monomer. All experiments were done at 627 nm red LED light, where dibenzoylferrocene shows no absorption.
- All surfaces in contact with the adhesive that are not acid-treated may cause uncontrollable polymerisation, namely the mixing container, stirrer, aluminium pan, PET film and any other equipment.
- Sample preparation (mixing and weighing estimates) should be done in a dry nitrogen environment to avoid contamination with impurities from the atmosphere.
- The rate of evaporation of the cyanoacrylate monomer becomes relatively high at elevated temperatures (see isothermal TGA data, Figure 34).
- The evaporation of the cyanoacrylate monomer causes blooming (frosting) of the polycarbonate window on the DSC head, affecting the intensity of light reaching the sample.
- The LED light source was given a cold start (i.e. light was not left to stabilise before measurement) to simulate actual adhesion conditions.
- The Loctite 454 is a gel that traps small bubbles during the mixing process and these are difficult to remove even by vibration.
- The dimensions of the DSC aluminium pan have an effect on the shape of the isotherm believed to be due to the scattering (absorption/reflecting) of light on the sides of the differently shaped pans (Pappas, 1992: 72).

Because of the uncontrollable variation in measurements, each DSC curve in this investigation is the average of ten runs done under the same experimental conditions.

4.2.2 Effect of photoinitiator concentration

The concentration of the photoinitiator (PI) will determine the kinetics and rate of polymerisation. The weight percentage of dibenzoylferrocene was changed for each sample, and repeated at different film thicknesses. Since the idea was to simulate actual underwater bonding conditions, relatively thick films (0.5 - 1.2 mm) were tested to determine the optimum PI concentration.



The technique used by Le (cited in Pappas, 1992: 76) shows the time required to attain 95% of the conversion. The shortest time, t_{95} , to reach 95% conversion with the highest value for ΔH yields the optimum PI concentration. The exotherms measured at a film thickness of 0.8 mm show how H_{max} increases and then decreases with increasing PI mass concentration (see Figure 35). At low concentration the time to reach H_{max} is slow because the concentration of the anionic PI is too low to effectively neutralise the acid stabilising the cyanoacrylate adhesive and initiate the polymerisation.



Figure 35: Exotherms for Loctite 454 with different PI concentrations

At high PI concentrations H_{max} is reached in a very short time, but the exotherm 'tails out' taking a long time to return to the base line. This is attributed to excessive light absorption by the outer layers hampering photo-initiation of the deeper layers, the so-called "the inner filter effect". Similar exotherms trends were observed for experiments conducted with adhesive film thicknesses 0.5 and 1.2 mm. Nevertheless the overall heat of reaction was independent of initiator concentration and film thickness and amounted to 262 ± 4 J/g.



The shortest time, t_{95} , to reach 95% conversion for the different film thicknesses measured is plotted versus PI concentration in Figure 36. A time scale is not provided for Figure 36 because the sample mass is different for each film thickness. As expected, the thinner the film, the shorter t_{95} was measured. The optimum concentration of dibenzoylferrocene for the polymerisation of film between 0.5 and 1.2 mm thick is in the range of 0.1 to 0.3 mass % PI.

The average bond line thickness measured during tensile testing was about 0.2 mm or less. A PI concentration in the order of 0.3 mass % or a little higher would probably increase the measured curing rate.



Figure 36: Time (t₉₅) for different PI concentrations and film thicknesses

Underwater surfaces can be rather rough due to corrosion therefore thicker bond lines can be expected on such surfaces. It was decided to use 0.2 mass % PI to have a good balance between a high curing rate and good light penetration into the thicker bond lines.

4.2.3 Effect of photopolymerisation temperature

Isothermal photopolymerisation experiments were performed at temperatures of -10, 20 and 50 °C (see Figure 37). Because of the poor reproducibility of the data, the average exotherm of ten samples at each temperature was taken.

The exotherms in Figure 37 show very different overall kinetic features. The lower the reaction temperature, the faster the overall polymerisation reaction precedes, with ΔH_{max} being larger and the time to reach ΔH_{max} being much shorter. This inverse temperature dependence has been shown by Pepper (1980) to occur with cyanoacrylates initiated by amines, including pyridine and derivatives, and aliphatic amines. It is also been shown that with photoinitiated ferrocene derivatives the polymerisation rate reduces as the temperature increases (Chan *et al.*, 2007 and Tanabe *et al.*, 2006)



Figure 37: Exotherms (typical average) at -10, 20 and 50 °C

A more in-depth kinetic study on the effect of temperature on the photoinitiation of cyanoacrylates is required to confirm these results but it seems likely that this





underwater adhesive will cure faster in very cold water conditions, giving it an advantage over most other underwater adhesives (epoxies) which fail to polymerise under such conditions.

It is arbitrarily assumed (see justification below) that the cure kinetics are described by a single Arrhenius factor as in the autocatalysed reaction described by Pappas (1992: 73):

$$\frac{d\alpha}{dt} = k' f(\alpha)$$
[10]

where

 α = degree of conversion

k' = Arrhenius-type reaction rate constant.

For isothermal conditions, Equation 10 can be integrated:

$$F(\alpha) \equiv \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = k' \int_0^t dt$$
[11]

At time t_{95} , 95% conversion is reached and therefore:

$$\alpha_{95} = \frac{Area \ at \ t_{95}}{Area_{total}}$$
[12]

Where the area reflects the integrated heat of reaction as determined by the DSC run. Substituting into equation 11 gives:

$$k't_{95} = F(\alpha_{95}) = \text{constant}$$
[13]

In this case the value of k' is given by the Arrhenius relationship:

$$k' = A \exp(-E_a / RT)$$
[14]



where

E_a = overall activation energy

- A = overall frequency factor
- R = ideal gas constant

T = absolute temperature (K).

From equations 13 and 14 the following relation is derived:

$$\ln(t_{95}) = \ln\left(\frac{\text{constant}}{A}\right) + \frac{E_a}{RT}$$
[15]

The Arrhenius plots of $In(t_{95})$ versus 1 000/T (K) are shown in Figure 38.

The DSC data provided clear evidence that there are in fact two reactions (or more) involved in the curing of the adhesive and that these reactions are probably independent, with each having its own activation energy. The above analysis considered only the state at 95% conversion. The fact that a reasonable fit is obtained with the assumption of a single Arrhenius factor may imply one of two things: either the activation energies of the two reactions are in fact the same (unlikely!) or the second reaction controls the process for high conversions, i.e. the first reaction is already complete.





Figure 38: Arrhenius plots of In(t₉₅) versus 1 000/T (K)

The Arrhenius plot shows that the time to reach 95% conversion is higher (slow polymerisation) at high temperature, as shown in Figure 37. The straight-line fit confirms the Arrhenius temperature dependence. The exotherms measured at low temperatures have better reproducibility than those measured at higher temperatures, as can be seen from the standard deviation error bars (see Figure 38). The cause of the high irreproducibility could be a combination of different factors, with evaporation of the sample being one of the main concerns. The overall activation energy E_a was calculated to be 6.5 kJ/mol.

4.3 Bond Strength Results

The shear bond strength was measured using the method described by the American Society for Testing and Materials (ASTM D4501 - 01) and the results are discussed in this section. A copy of the ASTM method, giving more information regarding the testing, is attached as Appendix C.

The following effects on shear bond strength were measured:

Illumination time



- Substrate material
- Water temperature
- Underwater work time
- Water ageing of bonds in potable water and sea water.

Each effect is discussed in more detail in the subsections below.

4.3.1 Illumination time

The effect of illumination time in potable water at 15 °C is shown in Figure 39. Substrate preparation was kept constant, with the top and bottom substrates both being polycarbonate. Illumination time was varied as shown in Figure 39. Shear bond strength was measured at room temperature. A minimum of five tests were performed for each data point shown in Figure 39.

An increase in bond strength with increased illumination time is observed for the first 50 seconds, after which constant bond strength is reached. An additional advantage offered by the cyanoacrylates over standard acrylic adhesives is initial bond strength without illumination, using its standard curing mechanism, in areas of intimate contact between the substrates. This is illustrated by the initial bond strength obtained without illumination in this investigation. However, the strength is also affected by the roughness of the substrate surface (contact area).

Further initiation is then accomplished by the added photoinitiator on illumination of the thicker and partially cured cyanoacrylate sections, shown by an increase in bond strength for up to 50 seconds of illumination (bond line thickness of 0.2 mm). No further increases in the measured shear bond strength are recorded with increased illumination after this time.

The time evolution of bond strength, whether it is peel or shear strength is influenced by a number of complex physical processes (Focke & Van Eeden, 1991):

• Plastic flow of the adhesive between the substrates from pressure and heat to fill crevices and cracks at the interface (physical bonding);

- Diffusion, absorption / desorption, and phase separation due to residual solvents and contaminants in the adhesive;
- Chemical curing of the adhesive to develop mechanical strength via crosslinking (cohesive strength in the bulk adhesive) and formation of chemical bonds between the substrate surface and adhesive (chemical bonding, adhesion).



Figure 39: Dependence of shear bond strength on illumination time

The constant bond strength reached after 50 seconds is directly related to the degree of cure reached under the specific bonding conditions. Shorter illumination times can be achieved using more powerful light sources or by thinner bond line thickness. The photoinitiator concentration was kept constant at 0.2% for all bond strength measurements, but it should be kept in mind that the optimum photoinitiator concentration is also related to the thickness of the bond line (Pappas, 1992: 6).

4.3.2 Substrate material

The different materials tested are categorised as follows:

- Metals
 - Mild steel
 - Aluminium
 - Anodised aluminium
 - Stainless steel 304
- Polymers
 - Acrylonitrile / butadiene / styrene ABS
 - Polyvinyl chloride PVC
 - Polymethyl methacrylate PMMA
 - Polycarbonate PC
 - Fibre-reinforced polyester (fibreglass) FRP

The overall shear bond strengths to substrate materials are shown in Figure 40.





*Severe failure of the substrate surface

Figure 40: Shear bond strength on different substrate materials

The adhesive's ability to bond to different substrate materials is affected by various features of the particular substrate, such as its hydrophobic or hydrophilic nature, its surface preparation and many other factors. The substrate materials are categorised into two groups: metallic and non-metallic or polymers.

It is clear that adhesion to polymeric substrates is much higher than to metallic substrates. Each category is discussed in more detail below.

Metals

All the shear bond strength measurements were taken in 15 °C potable water. Substrate preparation was kept constant, with different types of bottom substrate being used in each test. Illumination time was 1 minute in all the tests conducted. Shear bond strength was measured at room temperature.





Figure 41: Shear bond strength on metals

The minimum number of tests per substrate was five. The average shear bond strength of the cyanoacrylate adhesive (Loctite 454) on metals is given in Figure 41. The maximum and minimum shear bond strengths are illustrated using the error bars on each column.

The failure mode of each bond formed on mild steel and aluminium was adhesion failure between the metal surface and the cured adhesive layer. After bond failure, a film of water on the metal surface indicated that water was trapped, probably between the adhesive layer and the bottom substrate. The average shear bond strength was low, measured at 0.86 MPa and 0.49 MPa for mild steel and aluminium respectively.

The bonds made to aluminium anodised with sulphuric acid were, however, much stronger, measured at 1.27 MPa – more than double the strength than on untreated aluminium. Failure occurred mainly between the anodised layer and the metal surface, revealing the shiny metal surface underneath the grey anodised layer (see Figure 42).

Results and Discussion





Figure 42: Bond failure on aluminium anodised with sulphuric acid

A small amount of orange adhesive and grey anodising is still visible in Figure 42 on the anodised aluminium surfaces, showing partial cohesive failure and failure between the anodising and adhesive layers. Kinloch (1981: 233) also reported this failure mode of aluminium surfaces anodised with sulphuric acid

Adhesion to stainless steel 304 is even better than to anodised aluminium, measured at 1.70 MPa. This could be due to the fact than stainless steel 304 has very little oxide formation on its surface. The failure mode is partly cohesive failure and partly adhesive failure, with small amounts of adhesive still being present on the stainless steel surface after bond failure.

Polymers

The adhesive showed a much higher adhesion to immersed polymeric materials, namely ABS, PVC, PMMA, PC and FRP, than to metals (see Figure 43).





*Severe failure of the substrate surface

Figure 43: Shear bond strength on polymers

All the bonds made to polymers showed different degrees of cohesive failure (see Figure 44), except for the FRP which showed massive substrate failure. The average shear bond strength to polymers is in the order of 5 MPa.

The centre portion in Figure 44 is the inactive polyethyl cyanoacrylate (PECA) skin which reacted with the water and therefore could not (weakly bonded) bond to the polycarbonate bottom substrate. The white middle section and the white coral-like growths at the corners are indications of water polymerising the cyanoacrylate adhesive. The orange section, which is the photo-cured adhesive that remained on the bottom polycarbonate after bond failure, indicates cohesive failure.

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Figure 44: Cohesive failure to polycarbonate

One can therefore conclude than the average cohesive strength of cyanoacrylate adhesive (Loctite 454) applied and photo-cured underwater is about 5 MPa.

Drain *et al.* (1984 and 1985) found than cyanoacrylates dissolve polycarbonate to form a type of welded interface that withstands moisture over long periods. Whether cyanoacrylate adhesives have the ability to do the same to other polymers like ABS, PVC, PMMA and FRP is not clear, but very high bond strengths were obtained on these materials.

The large difference in shear bond strength between metallic and polymeric materials could be attributed to their respective hydrophilicities. Metallic surfaces tend to be more hydrophilic and polymeric surfaces more hydrophobic. It is more difficult for the cyanoacrylate adhesive to displace the water from immersed metal surfaces and ensure the good initial contact necessary for the development of strong bonds. However, the higher bond strength measured on stainless steel 304 with little or no oxide layer could also support the theory that hydration of the carbon steel and



aluminium oxide layers causes weak bonding to the respective substrates. The anodised aluminium surface is less susceptible to hydration damage, causing higher bond strength.

The average bond thickness on all of the substrates was about 0.2 mm measured with a micrometer after adhesion. The thickness can also be calculated because all substrates were bonded with 0.5 g of adhesive on a 2 500 mm² bonding area. The calculation is as follows:

Mass of adhesive = 0.5 gDensity of Loctite 454 = 1.1 g/cm^3

The volume of adhesive per bond is therefore:

$$V = \frac{m}{D} = \frac{0.5 \text{ g}}{1.1 \text{ g/cm}^3} = 0.4545 \text{ cm}^3 \text{ or } 454.5 \text{ mm}^3$$

It is assumed that the adhesive is spread uniformly over the entire 2 500 mm² bond area and that no adhesive is lost by squeezing out from under the substrate. The substrate surface is also assumed to be very smooth. The bond thickness will then be:

Bond Thickness =
$$\frac{\text{Volume}}{\text{Area}} = \frac{454.5 \text{ mm}^3}{2500 \text{ mm}^2} = 0.18 \text{ mm}$$

The measured average bond thickness is a little thicker (0.2 mm) than the calculated thickness because the adhesive did not spread to the absolute points of the corners of the square substrate. Therefore, the effective bond area is even smaller than expected.

4.3.3 Effect of water temperature on bonds

The shear bond strength at potable water temperatures between 1.5 and 40 °C was tested. Substrate preparation was kept constant, with polycarbonate used for the



bottom substrate. Illumination time was 1 minute in all the tests conducted. Shear bond strength was measured at room temperature. A minimum of five tests were performed for each data point shown in Figure 45.



Figure 45: Effect of temperature on shear bond strength

Water temperatures between 1.5 and 40 °C do not significantly influence the bond strength. Photo-DSC data revealed negative temperature dependence and therefore the rate of cure is lower at high temperatures, but this did not affect the bond strength at 40 °C. It can therefore be concluded that the 1-minute illumination of a bond 0.2 mm thick at 40 °C cured the bond fully before m easurements of the shear bond strength were conducted. This correlates with the working temperature for pure Loctite 454 (see data sheet, Appendix D) which can be used at between 0 and 40 °C, with only a small reduction in bond strength as the temperature increases.

4.3.4 Underwater work time

Unlike acrylate adhesives, cyanoacrylates are constantly reacting with the surrounding water when submersed. On submersion, the outer layer of the cyanoacrylate adhesive (clear light orange colour) rapidly polymerises to form a white protective skin. This skin is permeable to water and the diffusion of water slowly

polymerises the remaining adhesive inside the protective skin until all of it has been consumed (see Figure 46).



Figure 46: Water polymerisation of CA adhesive on a PC top substrate

Therefore water diffuses into the porous polyethyl cyanoacrylate (PECA) network skin (which looks like coral under a microscope), and then reacts with the ethyl cyanoacrylate (ECA) at the ECA / PECA interface. A pseudo-steady-state diffusion model may be used to describe the diffusion path, but this is outside the scope of this investigation. For this investigation, it was estimated that in room-temperature potable water the PECA skin grows to about 1.5 mm thick in 1 hour.

It should therefore be kept in mind that the bond should be made as soon as possible after submersion (water contact). The 0.5 g (\pm 0.01 g) of adhesive inside a 19-mm-diameter ring (see Figure 46) on the top substrate block with an average thickness of 1.6 mm was submersed in potable water at 15 °C for different submersion times. The submersed adhesive on the top substrate was then used to form a bond underwater.

The percentage reduction in shear bond strength is measured as a function of submersion time, as shown in Figure 47.



Figure 47: Effect of underwater work time on shear bond strength

The same experiment was also conducted in artificial sea water called "Ocean Fish" by Prodac. A slightly faster reduction in bond strength was measured in sea water due to the greater anion concentration of the dissolved salts which cause a higher pH than that of potable water (pH 7). This was also found by Katti & Krishnamurti (1999) who concluded that the rate of polymerisation of alkyl cyanoacrylates is higher in higher pH environments.





Figure 48: Reduction of bond area with increased work time underwater

The reduction in bond strength is due to a combination of two factors: the reduction in the amount of adhesive available for bonding and therefore a smaller bonding area, and the increase in bond line thickness due to the PECA skin which becomes thicker over time, preventing the two substrates from being sandwiched closely together (see Figure 48).

4.3.5 Ageing of underwater bonds

Water ageing of bonds made to steel and polycarbonate was tested in pure shear mode at regular intervals over a period of one month. The bonds were stored in both potable water and sea water at 17 $^{\circ}$ C under dark conditions. It was found that the bonds made on both steel and polycarbonate undergo a large reduction in shear bond strength within the first 50 hours of submersion. This is in contrast to what occurs with cyanoacrylate bonds made above water onto steel and polycarbonate and then exposed to high humidity for a month. Drain *et al.* (1984) reported on



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humidity aging of the bond strength of steel-steel cyanoacrylate bonds and stated that such systems rapidly lose most of their bond strength, whereas under similar conditions polycarbonate-polycarbonate bonds remain virtually unaffected (see Figure 15, Section 2.6.2).

Drain *et al.* (1984) concluded that the rapid loss of bond strength is caused by water vapour diffusing through the metal oxide/adhesive interface, causing weakening of the metal oxide layer due to the growth of ferric oxide. The strength may also be reduced by hydrolytic degradation of the adhesive or the possible displacement of the adhesive from the bonding surface by water molecules, commencing at the interface and progressing towards the centre of the assembly

Bonds between polycarbonate substrates are less susceptible because, obviously, no oxide layer is present and no real substrate/adhesive interface is formed because of dissolution of the polycarbonate in the ethyl cyanoacrylate monomer. Bond displacement and hydrolysis are therefore not possible because no interface is present (Drain *et al.*, 1985).



Figure 49: Ageing of underwater steel bonds





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In this investigation, both steel and polycarbonate showed a large reduction in strength during the first 50 hours of submersion (see Figure 49 and Figure 50). However, the modes of bond failure must be different. The steel bonds showed adhesive failure along the adhesive–steel interface, while the polycarbonate bonds showed cohesive failure of the adhesive. The reduction in bond strength within the first 50 hours is therefore due to a combination of factors. On steel, it is believed to be due to the displacement by water molecules along the interface and the weakening of the metal oxide layer caused by the growth of ferric oxide which occurs very rapidly. This reduction in strength occurs much faster than that observed by Drain and co-workers because the bond was made underwater and the adhesion does not need to progress towards the centre of the bond.

The cyanoacrylate adhesive dissolves the polycarbonate ('welding') as effectively as above water, giving the typical cohesive failure observed. It is, however, believed that hydrolytic degradation of the adhesive is also accelerated by making the bond underwater, which is responsible for the decrease in bond strength in the first 50 hours for polycarbonate joints. More testing is required to determine the true failure mode of joints made underwater.



Figure 50: Ageing of underwater polycarbonate bonds



Both the steel and polycarbonate bonds stabilised after the initial decrease in shear bond strength (first 50 hours). Thereafter, relatively constant shear bond strength was measured. No significant difference in the shear bond strength between potable water and artificial sea water was recorded. The polycarbonate bond strength in sea water is marginally stronger than in potable water, and the opposite is true for bonds made to steel.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

This chapter draws brief conclusions from the main results achieved, namely from spectroscopy and thermal analysis, and with regard to bond strength. A recommendation is made to guide future work.

5.1 Conclusions

A viable underwater adhesive system was developed for bonding polycarbonate sheet to other substrates. It is based on the commercial cyanoacrylate adhesive Locktite 454. This adhesive was cured photochemically using benzoylferrocene added at 0.2% (m/m). Very fast bond development was achieved by irradiation with blue (wavelength at 467 nm) LED lighting: the ultimate bond strength of adhesive films of 0.2 mm was achieved in less than 1 minute using a radiation intensity of ca. 5 mW/cm². Bond strengths varied with the nature of the substrate. The best performance was obtained when bonding one polycarbonate sheet to another; in this case the shear strength reached 5 MPa. The bond strength achieved is the same for water temperatures in the range of 1 to 40 °C. It was, however, most difficult to bond to metals. On anodised aluminium and stainless steel, the bond strength was ca. 1 and 2 MPa respectively. Water ageing of cyanoacrylates bonds on mild steel and polycarbonate show a decrease in bond strength during the first 50 hours after submersion. Thereafter the shear bond strength stabilises and remains approximately constant over a 30-day period.

A blue LED light source with a peak wavelength at 467 nm was chosen for curing as this wavelength is close to the absorption maximum for the initiator. Clear polycarbonate sheet also has a high transparency at this wavelength (86% at a thickness of 10 mm). This sheet thickness was used as the window in the photo differential scanning calorimetry (Photo-DSC) experiments to initiate adhesive cure. It was found in the DSC experiments conducted at 15 °C that the optimum initiator concentration is in the range of 0.3 to 0.1% (m/m) for films varying from 0.5 mm to 1.2 mm respectively. An advantage of blue light initiation is that it also enables polymerisation of thicker adhesive sections.



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Photo-DSC under isothermal conditions was used to determine the optimum photoinitiator concentration and to examine the effect of temperature on the curing kinetics. The photoinitiated DSC cure studies revealed complex cure behaviour. It appears that at least two separate cure reactions occur. Furthermore, the measured cure rates were not sufficiently repeatable to allow a proper kinetic analysis of the data. Thus only the near-complete cure condition (95% conversion) was considered. The polymerisation rates at -10, 20 and 50 °C were determined. The photoinitiation with dibenzoylferrocene showed negative temperature dependence and therefore the rate is faster at -10 °C than at 50 °C. The 95% conversion condition could be described by the temperature dependence of a single Arrhenius rate constant. In any case, the time to reach this state is the one that is of practical importance. Interestingly, the observed activation energy is negative, confirming that full cure is achieved faster at lower temperatures.

Thermogravimetric analysis (TGA) showed that Loctite 454 contains about 5% (m/m, fumed silica) filler. It also revealed that the adhesive is highly volatile: the rate of evaporation was ca. 34 mg/m².s at 50 °C. This high evaporation rate could also be one of the factors responsible for the poor reproducibility of photo-DSC data, especially at high temperatures.

This study has confirmed that cyanoacrylates can form strong underwater bonds when the correct bonding procedure is followed. These adhesives react rapidly with water. Therefore, adhesive should be applied such that there is minimal surface area exposed to water. Fortunately, a protective polyethyl 2-cyanoacrylate skin forms at the adhesive–water interface and this reduces the rate of water penetration. In this regard, the use of the adhesive in a 'gel' rather than a liquid form helps to avoid excessive contact with water during application. The adhesive bond should be prepared within a work time of 10 minutes to avoid loss of strength due to the reaction with water.

The procedure used for underwater application of the adhesive is very important. Good bonds are achieved when the application is such that fresh adhesive is squeezed from underneath the protective skin which simultaneously pushes water away during application.



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5.2 Recommendation

The photo-DSC results should be verified by other analytical techniques that are not susceptible to the many experimental problems of the photo-DSC technique used in the analysis of cyanoacrylates, as also found by Pepper (1980).



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APPENDIX A: TENSILE TESTING DATA

	Temp. °C	1.5	5	10	15	20	30	40
	Test 1	11.54	10.48	9.49	11.29	12.85	10.15	10.26
	Test 2	13.15	12.25	12.53	11.56	11.01	11.50	9.53
454	Test 3	9.37	9.40	10.67	11.82	14.64	10.59	10.28
tite	Test 4	10.91	12.25	10.54	14.77	14.05	9.18	12.20
Loc	Test 5	10.45	10.00	-	-	8.76	12.66	11.90
	Average							
	(kN)	11.08	10.88	10.81	12.36	12.26	10.82	10.83
	Test 1	5.21	4.73	4.28	5.09	5.80	4.58	4.63
	Test 2	5.93	5.53	5.65	5.22	4.97	5.19	4.30
454	Test 3	4.23	4.24	4.81	5.33	6.61	4.78	4.64
tite	Test 4	4.92	5.53	4.76	6.66	6.34	4.14	5.50
Loc	Test 5	4.71	4.51	-	-	3.95	5.71	5.37
	Average							
	(MPa)	5.00	4.91	4.88	5.58	5.53	4.88	4.89
	Bond Area							
	(mm²)	2 216						
	Standard							
	Deviation	0.63	0.59	0.57	0.73	1.08	0.60	0.52

Table 6: Temperature effect of shear bond strength data

Table 7: Effect of illumination ti	ime on shear bond strength
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	Time							1 min	2 min
		0	10	15	20	30	45	60	120
	Test 1	2.69	6.06	6.74	9.69	11.24	12.15	11.29	9.12
	Test 2	1.75	5.57	5.67	12.34	11.27	10.23	11.56	8.77
454	Test 3	2.05	7.71	9.42	10.31	12.05	9.54	11.82	11.63
tite	Test 4	2.72	6.85	7.80	12.32	9.72	10.89	14.77	12.11
Loc	Test 5	-	9.11	10.78	9.05	10.75	14.19	-	12.54
	Average								
	(kN)	2.31	7.06	8.08	10.74	11.01	11.40	12.36	10.83
		•		•	•	•		•	•
	Test 1	1.21	2.73	3.04	4.37	5.07	5.48	5.09	4.12
	Test 2	0.79	2.52	2.56	5.57	5.09	4.62	5.22	3.96
454	Test 3	0.93	3.48	4.25	4.65	5.44	4.30	5.33	5.25
tite	Test 4	1.23	3.09	3.52	5.56	4.39	4.91	6.67	5.46
Loc	Test 5	-	4.11	4.86	4.08	4.85	6.40	-	5.66
	Average								
	(MPa)	1.04	3.19	3.65	4.85	4.97	5.14	5.58	4.89
	Bond	-		-	-	-		-	-
	Area								
	(mm²)	2 216							
	Standard								
	Deviation	0.22	0.63	0.92	0.68	0.39	0.83	0.73	0.79

Table 8: Shear bond strength to different substrate materials – Metals

Dand Strongth	Ctool	A	Anodised	Stainless
Bond Strength	Steel	Aluminium	Aluminium	Steel
Test 1	1.26	0.88	4.43	3.12
Test 2	2.24	1.41	2.02	4.28
Test 3	1.45	1.08	1.91	3.05
Test 4	1.53	0.87	3.83	4.46
Test 5	2.09	1.19	2.58	3.25
Test 6	2.33	0.77	1.43	3.41
Average (kN)	1.82	1.03	2.70	3.59
МРа				
Test 1	0.59	0.41	2.09	1.47
Test 2	1.06	0.66	0.95	2.02
Test 3	0.68	0.51	0.90	1.44
Test 4	0.72	0.41	1.81	2.10
Test 5	0.98	0.56	1.22	1.53
Test 6	1.10	0.36	0.67	1.61
Average (MPa)	0.86	0.49	1.27	1.70
Bond Area (mm ²)	2 116		•	
Standard Deviation	0.22	0.11	0.56	0.29
	Bond StrengthTest 1Test 2Test 3Test 4Test 5Test 6Average (kN)MPaTest 1Test 2Test 3Test 4Test 5Test 6Average (MPa)Bond Area (mm²)Standard Deviation	Bond Strength Steel Test 1 1.26 Test 2 2.24 Test 3 1.45 Test 4 1.53 Test 5 2.09 Test 6 2.33 Average (kN) 1.82 MPa 1.06 Test 2 1.06 Test 3 0.68 Test 4 0.72 Test 5 0.98 Test 6 1.10 Average (MPa) 0.86 Bond Area (mm²) 2 116	Bond Strength Steel Aluminium Test 1 1.26 0.88 Test 2 2.24 1.41 Test 3 1.45 1.08 Test 4 1.53 0.87 Test 5 2.09 1.19 Test 6 2.33 0.77 Average (kN) 1.82 1.03 MPa	Bond Strength Steel Aluminium Anodised Aluminium Test 1 1.26 0.88 4.43 Test 2 2.24 1.41 2.02 Test 3 1.45 1.08 1.91 Test 4 1.53 0.87 3.83 Test 5 2.09 1.19 2.58 Test 6 2.33 0.77 1.43 Average (kN) 1.82 1.03 2.70 MPa Test 1 0.59 0.41 2.09 Test 3 0.68 0.51 0.90 1.81 Test 4 0.72 0.41 1.81 1.22 Test 3 0.68 0.51 0.90 1.22 Test 4 0.72 0.41 1.81 1.22 Test 5 0.98 0.56 1.22 1.27 Bond Area (mm²) 2.116 2.116 2.56

Table 9: Shear bond strength to different substrate materials – Polymers

	Bond Strength	ABS	PVC	PMMA	PC	FRP
	Test 1	9.25	10.92	9.20	11.29	5.48
	Test 2	8.85	11.63	8.90	11.56	8.69
	Test 3	10.53	7.41	10.80	11.82	4.51
454	Test 4	9.58	9.24	13.03	14.77	5.15
tite	Test 5	9.39	9.41	12.89	12.15	3.25
Loc	Test 6	10.64	9.96	7.99	10.23	-
	Test 7	-	-	-	9.54	-
	Test 8	-	-	-	10.89	-
	Test 9	-	-	-	14.19	-
	Average (kN)	9.71	9.76	10.47	11.83	5.42
	МРа					
	Test 1	4.36	5.15	4.34	5.33	2.59
	Test 2	4.18	5.49	4.20	5.45	4.10
	Test 3	4.97	3.50	5.09	5.58	2.13
454	Test 4	4.52	4.36	6.15	6.97	2.43
tite	Test 5	4.43	4.44	6.08	5.73	1.53
Loc	Test 6	5.02	4.70	3.77	4.83	-
	Test 7	-	-	-	4.50	-
	Test 8	-	-	-	5.14	-
	Test 9	-	-	-	6.69	-
	Average (MPa)	4.58	4.61	4.94	5.58	2.55
	Bond Area (mm ²)	2116				
	Standard Dev	0.34	0.69	1.01	0.81	0.95

Table 10: Effect of underwater work time on bond strength

	Work Time							
	(min.)	0	10	20	30	40	50	60
	Test 1	11.29	10.47	10.19	8.54	6.24	6.28	2.56
4	Test 2	11.56	9.54	9.25	8.40	4.13	3.33	3.98
e 45	Test 3	11.82	9.31	6.43	8.01	5.81	2.20	0.80
octit	Test 4	14.77	10.23	9.59	7.83	6.41	4.03	1.25
Ľ	Test 5	-	11.37	9.27	8.14	5.88	4.93	0.65
	Average (kN)	12.36	10.18	8.95	8.18	5.69	4.16	1.85
	МРа							
	Test 1	5.33	4.94	4.81	4.03	2.94	2.96	1.21
4	Test 2	5.45	4.50	4.36	3.96	1.95	1.57	1.88
e 45	Test 3	5.58	4.39	3.03	3.78	2.74	1.04	0.38
octit	Test 4	6.97	4.83	4.52	3.69	3.02	1.90	0.59
Ľ	Test 5	-	5.36	4.37	3.84	2.77	2.33	0.31
	Average (MPa)	5.83	4.80	4.22	3.86	2.69	1.96	0.87
	% Strength							
	Reduction	0.00	17.60	27.63	33.79	53.94	66.38	85.04
	Bond Area							
	(mm²)	2 116						
	Standard Dev.	0.76	0.39	0.69	0.14	0.43	0.73	0.66
Loctite 454	Average (kN)MPaTest 1Test 2Test 3Test 4Test 5Average (MPa)% StrengthReductionBond Area(mm²)Standard Dev.	12.36 5.33 5.45 5.58 6.97 - 5.83 0.00 2 116 0.76	11.37 10.18 4.94 4.50 4.39 4.83 5.36 4.80 17.60 0.39	 9.27 8.95 4.81 4.36 3.03 4.52 4.37 4.22 27.63 0.69 	 8.14 8.18 4.03 3.96 3.78 3.69 3.84 3.86 33.79 0.14 	 5.69 2.94 1.95 2.74 3.02 2.77 2.69 53.94 0.43 	4.93 4.16 2.96 1.57 1.04 1.90 2.33 1.96 66.38	0 1 1 1 0 0 0 85

Table 11: Effect of bond ageing on steel in potable water

Time (h)							
	1	45	210	350	518	612	780
Test 1	1.26	1.05	0.78	0.85	0.66	1.15	1.18
Test 2	2.24	0.70	0.96	1.09	1.25	0.58	1.39
Test 3	1.45	0.82	0.73	0.37	1.10	0.88	1.01
Test 4	1.53	0.66	0.75	0.44	1.93	2.04	1.14
Test 5	2.09	0.74	1.45	0.59	2.95	1.14	0.75
Test 6	-	0.72	1.43	2.27	-	1.10	1.68
Average (kN)	1.71	0.78	1.02	0.93	1.58	1.15	1.19
МРа							
Test 1	0.59	0.50	0.37	0.40	0.31	0.54	0.56
Test 2	1.06	0.33	0.45	0.52	0.59	0.27	0.66
Test 3	0.68	0.39	0.35	0.17	0.52	0.41	0.47
Test 4	0.72	0.31	0.36	0.21	0.91	0.96	0.54
Test 5	0.99	0.35	0.68	0.28	1.40	0.54	0.35
Test 6	-	0.34	0.67	1.07	-	0.52	0.79
Average (MPa)	0.81	0.37	0.48	0.44	0.75	0.54	0.56
Bond Area (mm ²)	2116						
Standard Dev.	0.2	0.07	0.16	0.33	0.42	0.23	0.15

Table 12: Effect of bond ageing on steel in sea water

Time (h)						
	45	210	350	518	612	780
Test 1	0.46	0.27	0.54	0.85	0.73	1.09
Test 2	0.77	0.57	0.32	0.42	0.18	0.94
Test 3	0.71	0.27	0.23	0.39	0.45	0.50
Test 4	0.70	0.25	0.26	0.66	0.20	0.84
Test 5	0.68	0.54	0.31	0.66	0.26	0.73
Test 6	0.61	0.30	0.24	0.33	0.23	1.71
Average (kN)	0.65	0.37	0.32	0.55	0.34	0.97
МРа						
Test 1	0.22	0.13	0.26	0.40	0.35	0.51
Test 2	0.36	0.27	0.15	0.20	0.08	0.44
Test 3	0.33	0.13	0.11	0.19	0.21	0.24
Test 4	0.33	0.12	0.12	0.31	0.09	0.40
Test 5	0.32	0.26	0.15	0.31	0.12	0.34
Test 6	0.29	0.14	0.11	0.15	0.11	0.81
Average (MPa)	0.31	0.17	0.15	0.26	0.16	0.46
Bond Area (mm ²)	2 116					
Standard Dev.	0.05	0.07	0.05	0.09	0.10	0.20

Table 13: Effect of bond ageing on polycarbonate in potable water

Time (h)								
	1	12	45	210	350	518	612	780
Test 1	10.7	7.13	2.64	3.22	3.41	5.86	4.83	3.64
Test 2	11.1	8.56	6.86	4.27	5.37	5.23	3.97	3.96
Test 3	9.57	8.86	3.66	3.64	3.62	5.24	2.96	8.57
Test 4	9.01	9.18	4.62	5.57	4.44	4.01	5.93	7.18
Test 5	10.1	4.11	3.72	3.93	4.09	3.21	2.93	5.56
Test 6	-	-	3.63	4.17	3.42	5.31	4.43	6.55
Average (kN)	10.1	7.57	4.19	4.13	4.06	4.81	4.18	5.91
мРа								
Test 1	5.03	3.36	1.25	1.52	1.61	2.76	2.28	1.72
Test 2	5.23	4.04	3.23	2.01	2.53	2.47	1.87	1.87
Test 3	4.52	4.18	1.73	1.72	1.71	2.47	1.40	4.04
Test 4	4.25	4.33	2.18	2.63	2.09	1.89	2.80	3.39
Test 5	4.75	1.94	1.76	1.85	1.93	1.51	1.38	2.62
Test 6	-	-	1.71	1.97	1.61	2.50	2.09	3.09
Average (MPa)	4.76	3.57	1.98	1.95	1.91	2.27	1.97	2.79
Bond Area (mm ²)	2 116							
Standard Dev.	0.39	0.98	0.68	0.38	0.36	0.47	0.54	0.90

Table 14: Effect of bond ageing on polycarbonate in sea water

Time (h)						
	45	210	350	518	612	780
Test 1	5.34	4.95	5.45	3.34	4.19	4.73
Test 2	7.04	6.24	5.96	4.54	6.82	9.99
Test 3	4.91	5.56	8.00	3.44	6.45	6.26
Test 4	6.05	5.58	8.30	6.30	5.44	4.69
Test 5	5.30	2.46	3.77	7.30	6.52	5.93
Test 6	6.43	3.73	5.19	2.42	6.02	11.09
Average (kN)	5.85	4.75	6.11	4.56	5.91	7.11
MPa						
Test 1	2.52	2.33	2.57	1.58	1.98	2.23
Test 2	3.32	2.94	2.81	2.14	3.22	4.71
Test 3	2.31	2.62	3.77	1.62	3.04	2.95
Test 4	2.86	2.63	3.92	2.97	2.57	2.21
Test 5	2.50	1.16	1.78	3.44	3.08	2.80
Test 6	3.03	1.76	2.45	1.14	2.84	5.23
Average (MPa)	2.76	2.24	2.88	2.15	2.79	3.36
Bond area (mm²)	2 116					
Standard Dev.	0.38	0.66	0.82	0.89	0.46	1.30

APPENDIX B: PHOTO-DSC DATA

Isotherms at -10 °C – the average of 10 samples is represented by the thick black line.



Figure 51: Isotherms measured at –10 °C





Appendix B



Isotherms at 50 °C – the average of 10 samples is represented by the thick black line.



Figure 53: Isotherms measured at 50 °C

Appendix B



Isotherms for film thickness 1.2 mm with different photoinitiator concentrations measured at 15 $^{\circ}$ C.



Figure 54: Isotherms of photoinitiator concentration in 1.2 mm film

See text (Figure 37, Section 4.2.3) for isotherms film thickness 0.8 mm with different photoinitiator concentrations measured at 15 $^{\circ}$ C.





Isotherms for film thickness 0<u>.</u>5 mm with different photoinitiator concentrations

Appendix B

APPENDIX C: ASTM D4501 - 01



Designation: D 4501 - 01

Standard Test Method for Shear Strength of Adhesive Bonds Between Rigid Substrates by the Block-Shear Method¹

This standard is issued under the fixed designation D 4501; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes a procedure and fixture used to determine shear strengths of adhesives used to bond materials with moduli higher than the modulus of the adhesive. The size and shape of the specimens are variable within the physical restraints of the fixture.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards:

D 907 Terminology of Adhesives²

E 4 Practices for Force Verification of Testing Machines³

3. Terminology

3.1 Many terms used in this test method are defined in Terminology D 907.

4. Summary of Test Method

4.1 In this test method, blocks, plates, or disks are bonded together, and the maximum force to shear them apart is determined.

5. Significance and Use

5.1 This test method provides an estimate of the shear strength of an adhesive on various machinable and nonmachinable substrate materials. It is particularly applicable for testing bonds between ceramic, glass, magnet moldings, and plastic parts with one flat face where machining would be difficult or impractical.

² Annual Book of ASTM Standards, Vol 15.06.

6. Apparatus

6.1 *Testing Machine*, conforming to the requirements of Practices E 4, with a capacity of not less than 44 kN (10 000 lbf) in tension.

6.2 Shearing Fixture— Perform the tests by using a shearing fixture consisting of a holding block and a shearing tool (Figs. 1 and 2). The holding block can accommodate specimens up to 80 by 80 by 13 mm (3 by 3 by $\frac{1}{2}$ in.). For small specimens as shown in Fig. 3B, an adapter plate (Fig. 4) can be inserted into the holding block to keep the shearing blade within its guides and to locate the specimen under the clamp. The shearing blade can accommodate specimens up to 30 by 30 by 13 mm ($1\frac{1}{8}$ by $\frac{1}{2}$ in.).⁴

7. Test Specimens

7.1 Test specimens can be any size within the limits of the shearing fixture capacity, as given in 6.2. Suggested sizes are as follows:

7.1.1 Metal Blocks— 25 by 25 by 6 mm (1 by 1 by ¼ in.).
7.1.2 Ferrite or Ceramic Blocks—25 by 18 by 13 mm (1 by

3/4 by 1/2 in.).

7.1.3 Wood or Plastic Blocks—25 by 25 by 13 mm (1 by 1 by $\frac{1}{2}$ in.).

7.1.4 Glass Plates— 75 by 75 by 13 mm (3 by 3 by $\frac{1}{2}$ in.). 7.2 Prepare the adhesive and apply in accordance with the recommendations of the adhesive manufacturer. Assemble the adhesive-coated specimens, and bond them in accordance with the procedure under investigation.

Note 1—Assemble the thrust surfaces, where the straight-sided specimen contacts the fixture, so that they are parallel to the fixture within 0.005 in./in. (0.005 mm/mm). Center round or shaped specimens within the shear blade in such a way that a moment is not applied to the specimen during shearing.

7.3 Remove any flash or fillets on the loaded side prior to testing. Fig. 3 shows typical specimens after bonding.

7.4 Test at least five specimens for each test condition.

¹ This test method is under the jurisdiction of ASTM Committee D14 on Adhesives and is the direct responsibility of Subcommittee D14.40 on Adhesives for Plastics.

Current edition approved March 10, 2001. Published May 2001. Originally published as D 4501 – 85. Last previous edition D 4501 – 95.

³ Annual Book of ASTM Standards, Vol 03.01.

⁴ Detailed drawings of the fixture are available from ASTM Headquarters, 100 Barr Harbor Drive, West Conshohocken, PA 19428–2959. Order ADJD4501.

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FIG. 1 Shearing Tool

8. Procedure

8.1 Mount the shear fixture in the testing machine with the holding block on top.

8.2 Place the specimen in the shearing fixture in such a way that one of the adherends is engaged by the holding block and the other by the shearing tool (Fig. 5). Close the toggle clamp on the rear of the holding block to keep the specimen located against the back face (Fig. 6). (Some adjustment of the pad may be necessary to accommodate varying specimen thickness.)

8.3 Test the specimen using a crosshead speed of 1.26 mm/min (0.05 in./min). Record the maximum force sustained by the specimen.

9. Calculation

9.1 Express all bond strengths in megapascal (MPa) or pound-force per square inch (psi).

10. Report

10.1 Report the following information:

10.1.1 Complete identification of the adhesive tested, including type, source, and manufacturer's code numbers.



FIG. 2 Holding Block

10.1.2 Complete identification of the adherends used, including dimensions and orientation in the test fixture, and the method of cleaning and preparing the surfaces prior to bonding.

10.1.3 Quantitative application and bonding conditions used.

10.1.4 Average thickness of adhesive layer after formation of bond, within 0.2 mm, and the means of measurement.

10.1.5 Sample conditioning and environmental exposure.

10.1.6 The temperature at which the test was performed.

10.1.7 Number of specimens tested.

10.1.8 The maximum shear stress reached for each specimen.

10.1.9 Average shear strength.

10.1.10 The nature of the failure: cohesion, adhesion, or voids in the bondline. Report the average percent of each.

11. Precision and Bias

11.1 Precision and bias for this test method are being determined and will be available by April 2005.

12. Keywords

12.1 block-shear; rigid substrates; shear strength



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FIG. 4 Specimen Adapter Plate for Fig. 3B Specimen



FIG. 5 Specimen Loaded in Shearing Fixture



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FIG. 6 Rear View of Fixture with Specimen Clamped in Place

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APPENDIX D: LOCTITE 454 TECHNICAL DATA SHEET



PRODUCT DESCRIPTION

LOCTITE[®] 454 provides the following product characteristics:

	- Janoa Jano
Chemical Type	Ethyl cyanoacrylate
Appearance (uncured)	Clear to slightly cloudy, colorless to straw colored gel ^{LMS}
Components	One part - requires no mixing
Viscosity	High
Cure	Humidity
Application	Bonding
Key Substrates	Wood, Paper, Leather and Fabric
N	

LOCTITE[®] 454 is designed for the assembly of difficult-to-bond materials which require uniform stress distribution and strong tension and/or shear strength. The product provides rapid bonding of a wide range of materials, including metals, plastics and elastomers. LOCTITE[®] 454 is particularly suited for bonding porous or absorbent materials such as wood, paper, leather and fabric. The gel consistency prevents adhesive flow even on vertical surfaces.

TYPICAL PROPERTIES OF UNCURED MATERIAL

Specific Gravity @ 25 °C	1.10
Casson Viscosity, 25 °C, mPa·s (cP):	
Cone and plate rheometer	100 to 450LMS
Viscosity, Brookfield - RVT, 25 °C, mPa·s (cP):	
Spindle TC, speed 20 rpm, Helipath	18,000 to 40,000
Flash Point - See MSDS	

TYPICAL CURING PERFORMANCE

Under normal conditions, the atmospheric moisture initiates the curing process. Although full functional strength is developed in a relatively short time, curing continues for at least 24 hours before full chemical/solvent resistance is developed.

Cure Speed vs. Substrate

The rate of cure will depend on the substrate used. The table below shows the fixture time achieved on different materials at 22 °C / 50 % relative humidity. This is defined as the time to develop a shear strength of 0.1 N/mm² .

Fixture Time, ISO 4587, seconds:

Steel (degreased)	5 to 20
Aluminum	2 to 10
Zinc Dichromate	10 to 20
Neoprene	<5
Rubber, Nitrile	<5
ABS	2 to 10
PVC	2 to 10
Polycarbonate	10 to 40
Phenolic	2 to 10

Technical Data Sheet

LOCTITE[®] 454

May 200

Cure Speed vs. Bond Gap

The rate of cure will depend on the bondline gap. Thin bond lines result in high cure speeds, increasing the bond gap will decrease the rate of cure.

Cure Speed vs. Humidity

The rate of cure will depend on the ambient relative humidity. The following graph shows the tensile strength developed with time on Buna N rubber at different levels of humidity.



Cure Speed vs. Activator

A

Where cure speed is unacceptably long due to large gaps, applying activator to the surface will improve cure speed. However, this can reduce ultimate strength of the bond and therefore testing is recommended to confirm effect.

TYPICAL PROPERTIES OF CURED MATERIAL

fter 24 hours @ 22 °C	
Physical Properties:	
Coefficient of Thermal Expansion, ASTM D 696, K ⁻¹	80×10
Coefficient of Thermal Conductivity, ASTM C 177, W/(m·K)	0.10
Glass Transition Temperature, ASTM E 228, °C	120
Electrical Properties:	
Dielectric Constant / Dissipation Factor, ASTM D 150:	
0.10 kHz	2.65 / <0.0

0.10 kHz	2.65 / <0.02
1 kHz	2.75/<0.02
10 kHz	2.65 / <0.02
Volume Resistivity, ASTM D 257, Ω·cm	10×1015
Surface Resistivity, ASTM D 257, Ω	10×1015
Dielectric Breakdown Strength, ASTM D 149, kV/m	m 25



Adhesive Properties

TDS LOCTITE[®] 454, May 2004

5000

4000

After 24 hours @ 22 °C		
Lap Shear Strength, ISO 4587:		
Steel (grit blasted)	N/mm ²	18 to 26
	(psi)	(2,610 to 3,770)
Aluminum (etched)	N/mm ²	11 to 19
	(psi)	(1,595 to 2,755)
Zinc Dichromate	N/mm ²	4 to 10
	(psi)	(580 to 1,450)
ABS	N/mm ²	6 to 20
	(psi)	(870 to 2,900)
PVC	N/mm ²	6 to 20
	(psi)	(870 to 2,900)
Polycarbonate	N/mm ²	5 to 20
	(psi)	(725 to 2,900)
Phenolic	N/mm ²	5 to 15
	(psi)	(725 to 2,175)
Neoprene	N/mm ²	5 to 15
	(psi)	(725 to 2,175)
Nitrile	N/mm²	5 to 15
	(psi)	(125 10 2,115)
Tensile Strength, ISO 6922:		
Steel (grit blasted)	N/mm ²	12 to 25
	(psi)	(1,740 to 3,625)
Buna-N	N/mm ²	5 to 15
	(psi)	(1,740 to 3,625)
After 30 seconds @ 22 °C		
Tensile Strength ISO 6922		
Buna-N	N/mm ²	>6 QOLMS
Durid-IN	(nsi)	(≥1 000)
	(1901)	(,000)

TYPICAL PERFORMANCE OF CURED MATERIAL

TYPICAL ENVIRONMENTAL RESISTANCE

After 1 week @ 22 °C Lap Shear Strength, ISO 4587: Mild steel (grit blasted)





3000

Hours

Chemical/Solvent Resistance

1000

Aged under conditions indicated and tested @ 22 °C.

Environment		% of initial strength		
	°C	100 hr	500 hr	1000 hr
Motor Oil	40	85	85	75
Gasoline	22	100	100	100
Ethanol	22	100	100	100
Isopropanol	22	100	100	100
Freon TA	22	100	100	100
Heat/Humidity 95% RH	40	65	55	50
Heat/Humidity 95% RH on Polycarbonate	40	100	100	100

GENERAL INFORMATION

This product is not recommended for use in pure oxygen and/or oxygen rich systems and should not be selected as a sealant for chlorine or other strong oxidizing materials.

For safe handling information on this product, consult the Material Safety Data Sheet (MSDS).

Directions for use

- 1. For best performance bond surfaces should be clean and free from grease.
- 2. This product performs best in thin bond gaps (0.05 mm).
- Excess adhesive can be dissolved with Loctite cleanup solvents, nitromethane or acetone.

Loctite Material Specification^{LMS}

LMS dated May 20, 2004. Test reports for each batch are available for the indicated properties. LMS test reports include selected QC test parameters considered appropriate to specifications for customer use. Additionally, comprehensive controls are in place to assure product quality and consistency. Special customer specification requirements may be coordinated through Henkel Loctite Quality.

Henkel Loctite Americas +860.571.5100 Henkel Loctite Europe +49.89.9268.0

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Storage

Store product in the unopened container in a dry location. Storage information may be indicated on the product container labeling.

Optimal Storage: 2 °C to 8 °C. Storage below 2 °C or greater than 8 °C can adversely affect product properties. Material removed from containers may be contaminated during use. Do not return product to the original container. Henkel Corporation cannot assume responsibility for product which has been contaminated or stored under conditions other than those previously indicated. If additional information is required, please contact your local Technical Service Center or Customer Service Representative.

Conversions

 $(^{\circ}C x 1.8) + 32 = ^{\circ}F$ kV/mm x 25.4 = V/mil mm / 25.4 = inches N x 0.225 = lb N/mm x 5.71 = lb/in N/mm² x 145 = psi MPa x 145 = psi N·m x 8.851 = lb.in N·mm x 0.142 = oz.in mPa·s = cP

Note

The data contained herein are furnished for information only and are believed to be reliable. We cannot assume responsibility for the results obtained by others over whose methods we have no control. It is the user's responsibility to determine suitability for the user's purpose of any production methods mentioned herein and to adopt such precautions as may be advisable for the protection of property and of persons against any hazards that may be involved in the handling and use thereof. In light of the foregoing, Henkel Corporation specifically disclaims all warranties expressed or implied, including warranties of merchantability or fitness for a particular purpose, arising from sale or use of Henkel Corporation's products. Henkel Corporation specifically disclaims any liability for consequential or incidental damages of any kind, including lost profits. The discussion herein of various processes or compositions is not to be interpreted as representation that they are free from domination of patents owned by others or as a license under any Henkel Corporation patents that may cover such processes or compositions. We recommend that each prospective user test his proposed application before repetitive use, using this data as a guide. This product may be covered by one or more United States or foreign patents or patent applications.

Trademark usage

LOCTITE is a trademark of Henkel Corporation

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APPENDIX E: CHEMICAL STRUCTURES OF FERROCENES

