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Fast underwater bonding to polycarbonate using photoinitiated cyanoacrylate

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ABSTRACT

Rapid underwater bonding of clear polycarbonate to metal or plastic substrates at temperatures approaching 0 °C was studied. Bonding was achieved within minutes using ethyl 2-cyanoacrylate gel cured using the photoinitiator (dibenzoylferrocene) with a blue-LED light source. The optimum initiator concentration varied from 0.3% to 0.1 wt % for adhesive films 0.5 to 1.2 mm thick, respectively. The polymerisation rate shows a negative temperature dependence making it highly suitable for cold environments. The ultimate shear strength of the bonds was temperature independent and ranged from 1 MPa for metallic to 5 MPa for plastic substrates, respectively.

1. Introduction

Neat cyanoacrylate reacts rapidly when it comes in contact with water. It is therefore not generally used for underwater bonding. However, the cured resin is not much affected by exposure to water. Consequently, this adhesive finds interesting underwater applications including tagging of sea mammals [1] and mussels or scallops [2] and fixing coral to rocks underwater [3,4]. Numerous other applications are described in the patent literature [5–7].

This study considered the use of a commercial ethyl cyanoacrylate-based adhesive for underwater bonding of clear polycarbonate sheets to other substrates for use with a proprietary applicator system. The key idea of the applicator is to use the adhesive itself to rapidly displace any water present between the two substrates to be bonded. This is achieved by extruding the adhesive from a central application hole. The water displacement is best achieved using a high-viscosity adhesive. Suitable thickening agent, e.g. fumed silica, can be used to impart the required consistency. Previous studies [5] showed that the strongest bonds are achieved with thin adhesive layers. Thicker adhesive sections take longer time to cure and sometimes full cure is not achieved.

Since the present application requires rapid bonding of a clear polycarbonate sheet to flat underwater substrates, photoinitiated cure was a definite option. Photoinitiated curing of acrylate adhesives is well established [8–10] and commercial systems are available [11]. The advantage is that photoinitiated cure can be initiated on demand and that thicker adhesive sections polymerise to completion. Thus this study considered the addition of an anionic photoinitiator to the cyanoacrylate adhesives to act as the primary cure initiator.

Ferrocene is a transition metal complex that has been the subject of numerous investigations [12]. The photochemical characteristics of ferrocene and several of its derivatives have been studied exhaustively [13–15]. Kutal and Yamaguchi [16] identified dibenzoylferrocene as a preferred anionic photoinitiator for cyanoacrylates. It is insoluble in water and has a maximum absorption peak at 485 nm. This closely matches the 470 nm blue LED light sources used in underwater camphorquinone initiated acrylate systems [8–10]. This light source was therefore selected for used in the present study.

2. Materials and methods

2.1. Adhesives and substrates

A commercial ethyl cyanoacrylate gel (Loctite 454) was used without modification. Dibenzoylferrocene was supplied by Sigma Aldrich Chemicals and used without further purification as a solution in hexane. Sea water was simulated using the aquarium product “Ocean Fish” supplied by Prodac. All other chemicals used were obtained from Sigma Aldrich. Metal sheets (hot-rolled mild steel sheet (12% carbon), stainless steel 304, and aluminium) were cut into squares measuring 10 × 100 × 100 mm in accordance with ASTM D 4501. The bonding surfaces of the different metal substrates were sanded with 100 grit sandpaper and then cleaned with a lint-free cloth soaked in isopropyl alcohol. The sulphuric-acid anodised aluminium was used as supplied. All thermoplastic sheets were supplied by Maizeys. The fibreglass-reinforced polyester (FRP) sheet was cast using glass fibre and polyester resin supplied by Plastocure.

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2.2. Light sources and calibration

The light source unit was custom-designed and consisted of 144 LED's in a 12 × 12 array. Nichia Corporation (Model: NSPB 500S) 5 mm blue ultra-bright LED's were used. The whole system was sealed inside an acrylic box to allow underwater illumination of the substrates. The light source was powered by a Vanson Deluxe Universal Regulated DC Power Supply (Model RC-1200). The output was set at 12 V DC and the overall current measured was 750 mA. 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. In this investigation the adhesive was illuminated with the light source placed at a distance of 50 mm away. This distance was chosen to ensure overlapping of the individual LED light beams and to allow sufficient space to fit the experimental equipment between the light source and the adhesive samples. All adhesive samples were irradiated at an effective light intensity of 5 mW/cm^2.

2.3. Photodifferential scanning calorimetry (Photo-DSC)

Isothermal photopolymerisation studies were performed on a Perkin-Elmer DSC-7 differential scanning calorimeter and analyzed using Pyris software. An indium standard was used for calibration. The DSC head was modified with a single polycarbonate window covering both the sample and the reference cells as described by Pappas [17]. The polycarbonate window was regularly replaced because, over time, vapours from the cyanoacrylate samples affected its transparency. The blue LED light source was positioned at a distance of 50 mm above the measuring pans. The light source was switched on and off using a timer.

Cylindrical aluminium sample pans were used with depths of 0.5, 0.8, and 1.2 mm to control the sample thickness. Nitrogen was used as the purge gas. The instrument was allowed to stabilize at every set isothermal temperature before photocuring experiments commenced.

2.4. Tensile testing

The shear strength of the adhesive bonds between the rigid substrates was measured according to the ASTM D4501 shear block testing standard on an Instron 4303 tensile tester. The load cell had a maximum capacity of 25 kN in tension. Shear strength values reported here are averages of at least five replicates in accordance with the ASTM specification.

2.5. Bonding process

The application process is a vital factor that determines the ultimate strength of underwater bonds. In this study the top substrate was always a clear polycarbonate sheet. This allowed facile illumination of the adhesive sandwiched between the two substrates.

A 19 mm diameter pencil ring was drawn in the centre of the polycarbonate sheet used as the top substrate. A quantity of 0.50 g ($\pm$ 0.01 g) of adhesive was placed on this demarcated area. This was done to keep the surface area of the adhesive, exposed to water, constant. The bottom substrate was first submerged in water. It was left in the water bath for at least 5 min to allow temperature equilibration. The top substrate was then submersed into the water bath and pressed firmly onto the bottom substrate. This action caused the adhesive to flow radially outward and cover the entire bond area. Next, the light source was submersed. It was positioned at a distance of 50 mm away from the bond line and switched on to initiate cure.

It should be noted that rapid polymerisation of the cyanoacrylate resin ensues as soon as it comes in contact with water. However, this gives rise to a protective skin layer that acts as a barrier for further water ingress by diffusion [5,6]. Thus only the adhesive's outer surface (inside the 19 mm ring on the top substrate) is instantly affected by the exposure to water. This part of the cyanoacrylate adhesive, cured by the reaction with water, assumes a white colour. This contrasts with the orange tint of cyanoacrylate cured by the blue light radiation. Since the white-coloured skin represents already polymerised material, it does not contribute to the bonding of the bottom substrate. When the two sheets are pressed together, the protective skin ruptures and adhesive is squeezed out. The uncured adhesive displaces the water as it travels radially outwards between the two substrates. Only this part of the surface is responsible for the measured bond strength. The non-bonded water-cured skin region trapped between the two substrates had an average diameter of 21 mm. This inactive bond area (346 mm^2) was subtracted from the total bond area (2 500 mm^2) to give, on average, an active bond area of 2154 mm^2 for calculating the shear bond strength. The average bond line thickness was measured at 0.2 mm.

The effect of illumination time and water temperature on the ultimate bond shear strength was determined using polycarbonate as top and bottom substrates. The sheets were bonded in potable water. The effect of illumination time was determined using a water temperature of 15 °C. Next, the illumination time was kept constant at 1 min and the water temperature varied from 1.5 to 40 °C. Bond strength measurements to various other substrate materials were done on samples bonded in 15 °C potable water as well as in simulated sea water. The different materials tested are categorised as metals (mild steel, aluminium, anodised aluminium, stainless steel 304) and other polymers including ABS (Acrylonitrile-butadiene-styrene), poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), polycarbonate (PC), and fibreglass-reinforced polyester (FRP). Substrate preparation was the same in each case and an illumination time of 1 min was used throughout.

The effect of the length of time for which the adhesive was exposed to water before bonding studied by delaying the pressing together of the sheets for predetermined times. These tests were performed in potable and in artificial sea water at a temperature of 15 °C.

In all cases the actual shear bond strengths were measured at room temperature. The averages of at least five replications are reported.

3. Results and discussion

3.1. Thermal analysis

3.1.1. Experimental problems with Photo-DSC

The cure reaction of cyanoacrylates is highly exothermic and calorimetric techniques seem ideal to study the polymerisation kinetics. Cyanoacrylates are among the most reactive monomers to be examined kinetically. Pepper and co-workers [18,19] studied their cure kinetics and the mechanism of polymerisation. Despite the fact that they employed carefully controlled experimental conditions, problems were experienced with respect to reproducibility. Similar problems were experienced in this study where the polymerisation of cyanoacrylate adhesives was followed using photo-DSC.

3.1.2. Effect of photoinitiator concentration

It is conventional to assume that the DSC-measured heat flux is proportional to the rate of polymerisation. The amount of