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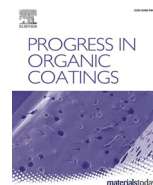
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Citation:

JANANI, R, MAJUMDER, Deblina, SCRIMSHIRE, Alex, STONE, A, WAKELIN, E, JONES, AH, WHEELER, NV, BROOKS, W and BINGHAM, Paul (2023). From acrylates to silicones: A review of common optical fibre coatings used for normal to harsh environments. *Progress in Organic Coatings*, 180: 107557. [Article]

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Review

From acrylates to silicones: A review of common optical fibre coatings used for normal to harsh environments

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ARTICLE INFO

Keywords:

Optical fibre coating
Acrylates
Polyimides
Silicone
Harsh environment

ABSTRACT

The full realisation of optical fibres in devices such as sensors is reliant on the stability of their polymer coating under in-service conditions. Depending on the application, resistance to several environmental factors may be required, such as high or low humidity level, temperature, pressure, or exposure to aggressive solids, liquids or gases. Changes in mechanical or chemical properties as a result of harsh environments can lead to stresses in the coating and subsequent deterioration of the physical or optical properties of the optical fibre. A variety of coating materials are available on the global market, offering optical fibre manufacturers a plethora of options. This review provides a comparison among four most utilised, commercially available types of coating material: conventional and specialty acrylates, polyimides and silicones. It details the history of their development, reported physiochemical properties and some of their main limitations in the context of optical fibre coating applications.

1. Introduction

1.1. Background

Optical fibres are one of the primary enablers of modern communications, facilitating the transmission of information at high-speed, over long-distances. Early precursors to modern optical fibres include Hopkins and Kapany [1], who in 1954, demonstrated that coherent bundles of glass fibres transmit light, originally with the scope of improving gastroscopy procedures and later used for the inspection of inaccessible railway bolts [2]. These early fibres suffered from high transmission losses (1000 dB/km) [3,4], which were found to be due to contaminants in the glass that could be removed to reduce attenuation [5]. In the mid-1960s, Corning Glass Works were able to reduce attenuation by $\approx 98\%$ to 16 dB/km⁶ by using a titanium doped high-purity fused silica fibre core [3]. Transmission losses were further reduced to 0.2 dB/km in 1979, and by 1982 Corning had achieved an attenuation of 0.16 dB/km [6,7]. In 2018, a 0.1419 dB/km loss fibre was reported by the Optical Communications Laboratory, Japan [8].

A standard single mode optical fibre used for telecommunications

consists of a core, cladding and a protective coating (Fig. 1). The core and cladding are usually made from fused (amorphous, glassy) silica (SiO₂), often incorporating low levels of dopants, such as Ge or F, to control the refractive index and minimise glass disorder. Despite the high inherent strength of pure silica, optical fibres are susceptible to abrasions, microbend losses and static fatigue in the absence of a protective coating [6,9,10]. Therefore, layers of coating are applied immediately after the newly drawn fibres exit the furnace in the drawing tower. The coating (with a thickness ranging from a few μm to $>100\ \mu\text{m}$) is then cured using heat or ultraviolet (UV) light. In early 1970s, a range of polymeric coatings (epoxy, acrylic and silicone-based) were explored for optical fibres [9,11]. UV-curable coatings, such as single-layer epoxy acrylates, became particularly popular in the 1980s. Dual-layer coating systems (particularly using urethane acrylates) were also introduced around this time to minimise bend losses [12–15]. The primary role of the secondary coating (outer layer coating) in a dual-layer system is to protect the primary coating against mechanical or environmental damages (e.g., moisture exposure). Depending on the application, the entire fibre may be encased in a protective jacket (as illustrated schematically in Fig. 1) to shield the fibre from the surrounding environment

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<https://doi.org/10.1016/j.porgcoat.2023.107557>

Received 22 November 2022; Received in revised form 7 March 2023; Accepted 20 March 2023

Available online 31 March 2023

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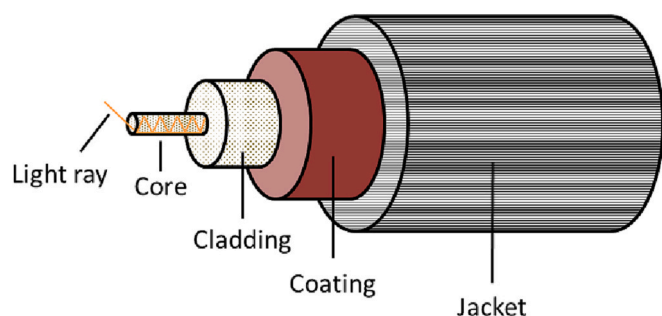


Fig. 1. Schematic of a typical optical fibre structure.

and to provide the fibre with added mechanical support.

Currently, a wide variety of fibre coatings are available on the market, the most common of which are acrylates, polyimides, and silicone-based coatings. Acrylate coatings used for optical fibres can be broadly categorised as “conventional” acrylates and “specialty” acrylates. The “conventional” acrylates (also known as telecom-grade acrylates) are commonly used for telecommunication applications and have a nominal upper temperature limit of 85 °C [15,16]. The “specialty” acrylates have a wide range of applications beyond telecommunications in a variety of sensors, high laser power transmission and in diagnostic medical devices. Specialty acrylates are a large family of acrylate polymers and for the context of the present work, the term “specialty” refers to modified acrylates with improved thermal and chemical stability in harsh environments compared to the “conventional” acrylates. While outside the scope of this work, it is worth noting that metallic coatings (e.g., gold, aluminium, copper) are another important category of coatings utilised for optical fibres. Metallic coatings have several advantages over acrylates, silicones and polyimides including their higher thermal and chemical stability as well as their resistance to nuclear radiation [17]. However, they can react with the silica core/cladding [18] or oxidise [19] at high temperatures. In addition, differences in thermal expansion coefficients between a metallic coating and the silica cladding can cause an increase in optical attenuation levels during heating or cooling cycles and thus, limits their application [20].

1.2. Application-driven considerations

Glass optical fibres are typically manufactured from silica (often including low levels of dopants), which in pure form has high tensile strength (≈ 14 GPa) [21] and thermal stability (up to 1000 °C) [22]. However, the presence of coating(s) is essential to protect the silica glass from abrasions and mechanical stresses, and from subsequent crack formation and propagation during installation. With the rapid growth in the field of lasers and optoelectronics since the 1970s and the expanding scope for optical fibre applications, came a fast-growing demand for durable optical fibres suited for operation in harsh environmental conditions [23,24]. Depending on the application, a harsh environment may be defined as extreme temperatures, pressures or humidity levels, exposure to aggressive chemicals, high mechanical strain, or a combination of these conditions [15,17,25–29]. For instance, Distributed Temperature Sensors (DTS) are widely utilised in gas and oil industries for remote temperature monitoring and detection of leaks in oil wells [26,30,31], exploiting the extended reach of optical fibres. These systems are often required to withstand extended exposure to temperatures as high as 380 °C [20,32]. While silica-clad fibres have a high potential for such applications [33], the thermal stability of optical fibres is limited by the coating used. Degradation of the coating material under such high temperatures can lead to an increase in bend losses and attenuation levels hence, negatively impacting the optical output [20]. In addition, geothermal wells are hydrogen-rich environments and thus, an effective barrier coating against hydrogen ingress and formation of hydroxyl groups within the interstices of silica is required to minimise

drop in the efficiency of the DTS system [20,30].

Furthermore, different applications require different fibre designs in terms of the transverse core and cladding refractive index profile. Some applications (for example, long-haul data transmission in the C-band) usually require ultralow loss, single-mode fibres, with a typical core diameter ~ 10.4 μm and a small refractive index difference between the core and cladding materials to ensure single mode behaviour (for example, Corning® SMF-28® Ultra Optical Fibre [34]). Other applications, such as high-power delivery, may require larger core multimode fibres, in order to improve their power handling ability. While in most cases the fibre will be designed such that there is minimal interaction between the guided light and the fibre's external coating, this interaction is dependent the fibre's transverse refractive index profile as well as the fibre's deployment condition. Principally, the coating is more susceptible to laser induced damage compared to the silica core/cladding and escape of light from the core, can lead to localised heating of the coating material due to light absorption [35]. This may be more likely in the case of very high laser power delivery or if the fibre is deployed in a tightly coiled condition where bend losses are increased [35,36]. Additionally, the refractive index of the coating itself can play an important role in the optical properties of the fibre. In applications such as fibre lasers, a ‘low-index’ coating material is applied, with a refractive index below the cladding material; in this case, the coating acts as a further cladding region, and enables transmission of light within the fibre's primary cladding which can be used to optically pump the fibre's core [37]. A low-index coating can also be used in applications where a high numerical aperture (which is related to the ability of an optical fibre to collect light [33]) is required.

It is also important that the protective coating is applied uniformly across the length of the fibre and is concentric around the core [38]. A suitable coating must have low surface tension, good adhesion to glass, and chemical and thermal durability [6]. During application, there may also be a need to splice optical fibres regularly to build the desired optical system which requires mechanical stripping of the fibre coating. While it is common to include an adhesion enhancer in the coating formulation [38], an ideal optical coating must have a sufficiently low strip force to enable ease of handling. According to GR-20-CORE,¹ a strip force in the range of 0.2 to 2.0 lbf (≈ 0.89 – 8.90 N) is desirable for optical fibre coatings [39,40]. Removal of a coating exhibiting a strip force >9.0 N can result in damage to the glass fibre [15].

Other considerations such as cost and availability, curing mechanism and curing rate, and mechanical strength must be taken into account during coating selection process [6,12,15,38–40]. Considering the broad range of coatings available on the market, there is a need for systematic studies providing comprehensive comparison among products with respect to different aspects of an optical fibre coating.

It is the purpose of this paper to provide the reader with a brief history of four commonly utilised optical fibre coatings with an emphasis on their origins, evolution, and key properties (such as chemical structure and versatility, curing rate, refractive index, strip force, etc.). Focus is then put on examples of their strength and shortcomings when exposed to different in-service conditions aiming to highlight some of the application-driven challenges and the rationale behind choosing alternative coatings. In the final section, a comparative overview is paired with a few examples of available products on the market today hinting at gaps in the field. This paper was put together by reviewing a number of sources including articles, reports, books, patents, and product specifications for coating materials (as cited). Multiple databases (Google Scholar, Web of Science, Scopus) and identifiers (such as keywords of this publication) were used to generate the initial list of relevant sources. Some of the sources were subsequently identified using the Snowball method. Sources were then examined and refined based on credibility, impact and relevance to the primary research questions.

¹ Generic requirements for optical fibre and optical fibre cable.

Greater weight was given to peer-reviewed articles published after 2000 and those written by well-known scientists in the field. For coating specifications (listed in the final section) Google was used as the main search engine and some manufacturers/distributors were contacted directly.

2. Conventional acrylates

2.1. Background, chemistry and curing mechanism

Acrylates or acrylic polymers offer a wide range of applications in products such as coatings, paints, adhesives, textiles, elastomers, and a shatter-resistant replacement for glass (e.g., PLEXIGLAS®). The term *acrylate* refers to a chemical group consisting of a C = C bonded to an ester functional group (– COOR). The huge commercial production, application and adaptation of acrylates by various industries is primarily due to their facile polymerization reaction via free-radical mechanism, their low cost, high transparency, good mechanical properties and ease of colouring and processing [41–45]. The presence of C = C bonds and their neighbouring electron withdrawing carbonyl groups (enhancing the reactivity of the double bonds) allows these materials to undergo prompt polymeric reactions with a variety of substrates [46–52].

Free radical/photopolymerization (FRP) is the most common method utilised for acrylate coating fabrication and consists of three fundamental steps: initiation, propagation, and termination [53]. To elaborate, the initiation step includes the formation of radicals and their subsequent reaction with existing vinyl monomer components of acrylates. The propagation step involves rapid and progressive addition of monomers to the growing polymer chain without any changes to the active centre of the enolate (ester component of acrylate). Finally, termination is the involvement of the growth active centres, usually by combination or coupling of the radicals of two growing polymer chains or by disproportionation. Additionally, a chain transfer might occur during this process, which contributes to the transfer of the growth active site from the active chain to an inactive one, a monomer or a solvent molecule. This process is reported to occur under the irradiation initiation of UV-, visible and in rare cases IR-light sources [54–56] but the UV-cure technique is most commonly utilised. During FRP, UV-light provides the energy to the vinyl acrylic moiety to act as initiator, resulting in polymerisation [55].

The unsaturated vinyl group present in acrylates actively participates in radical polymerization reaction to form new saturated C – H bonds (Fig. 2). The newly formed C – H bonds are particularly sensitive to the near infrared (nIR) region due to the decrease in corresponding force constants of the respective bond (double to single bond transformation) [57]. As a result of this sensitivity, several optical properties of the coated waveguide/optical fibre, including refractive index and light absorbency, can be impacted. Due to photoactivity of the vinyl group, photo-patterning of an acrylate substance can also be performed easily by applying localised radiation on the substrate of interest [57].

The monomers for acrylate polymers are esters of acrylic and methacrylic acid (Fig. 3a) [58,59]. The properties of acrylates are influenced by the inductive effect of the functional groups present (R and R'). Examples of some of the commonly used acrylate monomers are provided in Fig. 3b. Acrylate polymers (where R & R' = H) tend to be soft and tacky, while methacrylate polymers (where R' = CH₃) are hard and

brittle [58]. Adjustment of the amount of each type of monomer can yield co-polymers of desirable hardness and flexibility. Many commercially available acrylate polymers are copolymers of acrylic and methacrylic esters and are available under various trade names including Acrylite® [60], Europlex® [61], Duraplex® [61], and PLEXIGLAS® [62].

In late 1970s and early 1980s, UV-curable coatings became exceedingly popular for optical fibre protection against external mechanical stresses, abrasions and water diffusion [10,64]. UV-curable acrylates were one of the earliest reported polymer coatings used for optical fibres mainly due to their ability to facilitate a high fibre drawing rate [10,65–67]. In 1986, Rodas et al. [67] reported a ≈1.5-fold increase in fibre drawing speed and an improved water resistivity when a blend of UV-curable acrylate oligomers was used compared to a thermoset silicone coating.

In general, a UV-curable coating contains one or several oligomers, diluent monomers, photoinitiators and additives such as adhesion promoters, plasticizers and/or polymerisation regulator. For industrial coating applications, the desired coatings are prepared after careful selection of constituent oligomeric structures and their corresponding functionality. In the late 1970s and the early 1980s, epoxy acrylates were a common type of oligomer used in single layer optical fibre coating systems due to their versatile chemistry, high curing rate and good chemical resistivity [38,65]. These oligomers soon gave way to urethane acrylates in dual-layer coating systems to improve fibre resistance against microbend losses [68,69]. Depending on the molecular weight of the urethane oligomer used, coatings with different characteristics, ranging from soft with low Young's modulus to hard with high Young's modulus, were synthesised as the primary and secondary coatings, respectively [6,13,70].

2.2. Key properties and limitations

It has been shown that the precursor used for the synthesis of the acrylate oligomer can greatly impact the properties of the resultant coating [71,72]. For example, it was revealed that linear urethane oligomers based on rigid block polyols ensued urethane acrylate coatings with both higher modulus and toughness [71]. Numerous blends of different acrylate oligomers have been proposed to tailor the coating properties [73–76]. Blends of urethane and epoxy acrylate oligomers have been tested to fabricate coatings with high elastic modulus, abrasion resistance and flexibility to minimise microbend losses [67]. Shen et al. [74] prepared multiple acrylate-based coatings by combining epoxy, urethane and silicone acrylate oligomers. They demonstrated that an increase in the urethane acrylate content improved elongation of the coating (an attractive property for a primary coating) but prolonged the curing time while an increase in the proportion of the silicone acrylate oligomers showed the opposite effect. Increase in the proportion of the epoxy acrylate resulted in lower elongation but an increase in curing rate and tensile strength (higher tensile strength is favourable for secondary coatings). Inclusion of adhesion promoter(s) is common for acrylate coating formulations [5]. However, presence of certain oligomers (e.g., vinyl acrylate [77]) can eliminate the need for an adhesion promoter and expedite the curing process by reducing the viscosity of the mixture. Today, most of the commercially available acrylates are composed of a polyether or polyester backbone [15]. Although

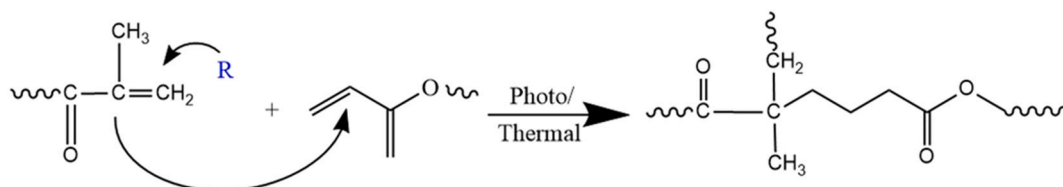


Fig. 2. Radical polymerisation of unsaturated vinyl group in acrylates.

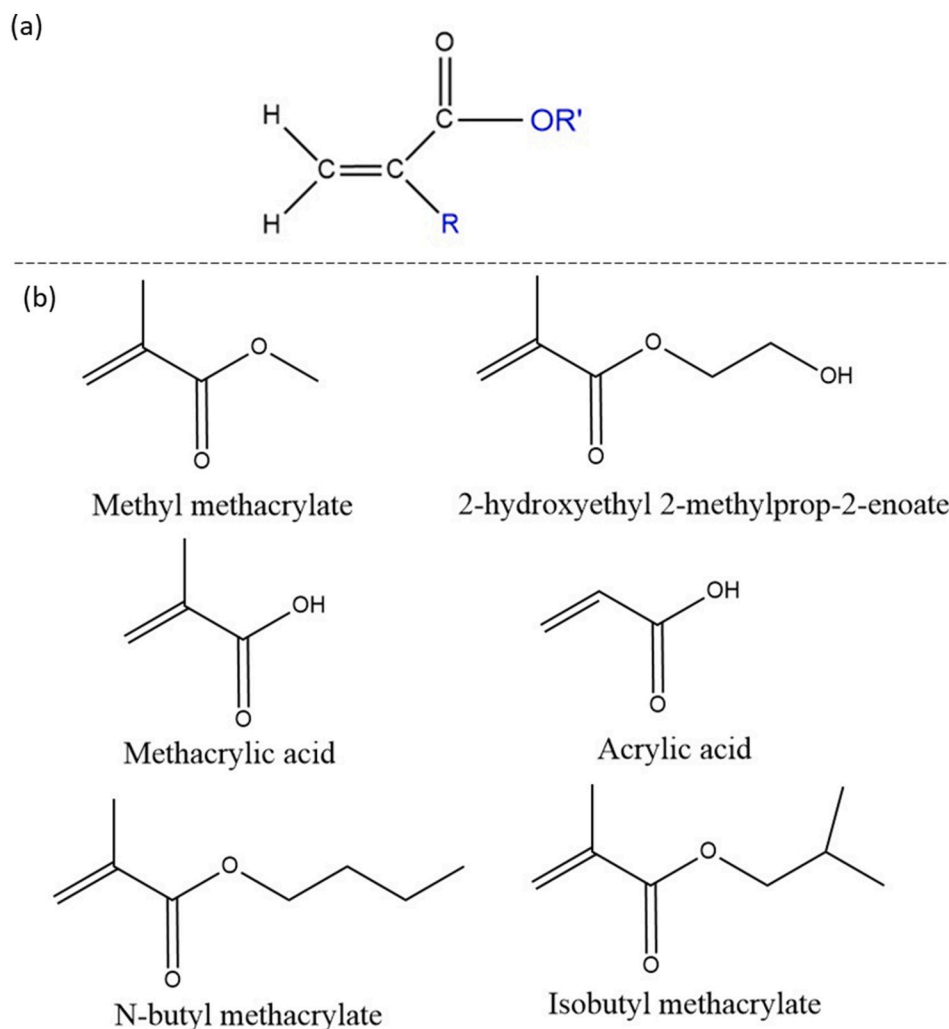


Fig. 3. (a) Representative chemical structure of acrylic ester, where R & R' = H for acrylates R = CH₃ for methacrylates, (b) Chemical structures of some commonly utilised monomers for acrylates synthesis [63].

polyethers offer excellent hydrolytic stability [78], they are less oxidatively stable compared to polyesters and are typically used with antioxidants [75].

There are several industrial standards and requirements (e.g., GR-20-Core [40]) in place to help assess the performance of optical fibres. These include (but are not limited to) changes in attenuation levels after temperature cycling and exposure to high temperature and humidity. Telecom-grade optical fibres are typically optimised for temperatures up to 85 °C, above which conventional coatings begin to degrade. It has been shown that prolonged aging of urethane acrylate oligomer resins at temperatures ranging from 85 °C to 115 °C (in both wet and dry conditions) can lead to deterioration of mechanical properties of these coatings [70]. Increase in fracture stress and decrease in Young's modulus are examples of changes reported and associated with oxidative or hydrolytic degradation of the polymer network. Degradation in the acrylate polymer backbone is often accompanied with yellowish to brownish discoloration in the coating [79]. Stolov et al. [15] compared the physical, thermal and optical properties of a series of fibres coated with commercial and "in-house" acrylate coating formulations. Although fibres coated in a dual-layer fashion with urethane acrylates showed good performance under ambient atmosphere, they were the first to degrade when exposed to harsh environments (dry and wet aging under air and N₂). Urethane acrylates are also outperformed by heat and UV-curable silicone coatings (when exposed to 200 °C in air) as reported by Sohma and Hattori [80]. Stresses in the coating caused by thermal

expansion/shrinkage, volatilisation of unbound components and scissions across the low heat resistant polymer backbone can lead to drastic changes in the breaking strength and Young's modulus of the coating causing an increase in microbend-induced optical losses. Therefore, conventional acrylates are not recommended for applications under adverse conditions.

With the discovery of photosensitivity in optical fibres [81] which led to the development of Bragg gratings for optical communication new challenges arose. Conventional fibre gratings are fabricated by irradiating a UV laser through a phase mask to generate periodic modification of the refractive index within the fibre core [82]. However, conventional acrylates are not UV-transparent which implies that the coating had to be stripped and recoated before and after UV radiation or done during fibre drawing on bare fibres [83]. Over time, the need for UV-transparent fibre coatings grew to simplify this process. Masson et al. [84] compared the performance of several commercially available aliphatic acrylate oligomers and photoinitiators to develop a highly reactive and UV transparent optical fibre coating. It was shown that a silicone acrylate coating, Ebecryl® 350 (Allnex, USA), had the highest deep UV transparency followed by a urethane acrylate coating, Laromer LR8987 (BASF, China). They further explained that the presence of carbonyl groups, urethane groups or any groups containing non-localised electrons can reduce UV transmittance.

Nevertheless, conventional acrylates remain very competitive on the market today with regards to cost, curing rate and chemical versatility.

Most conventional acrylate coatings have a refractive index in the range 1.46 to 1.57 [35,85] although this value can be tailored with the help of additives and specific functional groups (discussed in more detail in Section 3). In addition, acrylate coatings can be stripped mechanically with a typical strip force ranging between 2 and 8 N [15] allowing easy handling. The huge scope of modifications on acrylate base polymer coatings has launched the research area of specialty acrylates.

3. Specialty acrylates

3.1. Background

The demand for optical fibres able to withstand harsh in-service environments and adverse conditions has grown over the years. The ability to withstand water permeation and hydrogen diffusion was at the forefront of acrylates manufacturers' agenda in the 90s [86]. In the late 90s, the Environmental Protection Agency in The United States lifted restrictions on specialty acrylates production which opened the door to commercializing new and more advanced acrylates [87]. Modification of acrylate polymer chains with the help of various functional groups was explored by manufacturers around this time. In 1996, Alcatel Fibres Optiques (based in France) introduced a UV-curable urethane acrylate coating with fluorinated side chains [86]. Incorporation of fluorine in the acrylate oligomers enhanced the static fatigue value of the coated fibres and reduced their water permeability compared to fibres with AFC™ coating, a well-known Alcatel urethane acrylate coating. Fluorinated polyacrylates are one of the most promising types of specialty acrylates [88]. The impact of fluorine on optical attenuation was realised prior to the 90s and encouraged application of fluorinated alkyl acrylates as cladding for plastic optical fibres [89,90]. Apart from fibre optics, this class of polymers has found extensive applications for corrosion protection [91], protective coating in electronic applications [92], thin film coatings [93–96] and photolithography [97].

3.2. Key properties and limitations

It has been decades since fluoropolymers gained extensive attention for coating applications due to their outstanding chemical and thermal stability and low surface tension [33,98,99]. The high electronegativity and small atomic radius of fluorine atoms are responsible for the formation of short and energetic C–F bonds in fluoropolymers and their outstanding chemical and thermal durability [33,98,100]. Fluoropolymers have a small dipole moment which contributes to their reduced refractive index and low surface energy and surface tension [91,98,99]. Other properties such as their low dielectric constant, excellent chemical stability against typical solvents, hydrocarbons, acids, alkalis, and moisture adsorption have made fluoropolymers one of the most interesting materials for specialised applications [101–105].

It is known that the replacement of hydrogen atoms with fluorine can reduce optical losses caused by nIR absorption of C–H bonds [106,107]. Replacing methyl groups in methacrylates with fluorine atoms to form 2-fluoroacrylates can considerably reduce optical losses [108]. Use of materials composed of 2-fluoroacrylates and fluorinated aromatic groups in plastic optical fibres was shown to result in a higher onset T_g and decomposition temperature compared to that of polymethylmethacrylate or PMMA [108]. Fig. 4 shows the significant reduction in optical losses of fibres with poly(1H, 1H-perfluorocyclohexylmethyl 2-fluoroacrylate) compared to PMMA beyond 800 nm. It is worth noting that this fluorinated compound demonstrated lower Young's modulus (1500 MPa) compared to PMMA (3070 MPa) [108].

The presence of fluorinated acrylates in a coating mixture can also impact the refractive index of the coating material. In a systematic study, Glaesemann et al. [35] demonstrated the inverse linear relation between concentration of fluoroacrylate monomers and refractive index of acrylate-based cured coating films (composed of urethane acrylate oligomers and aliphatic acrylate co-monomers). They showed that the

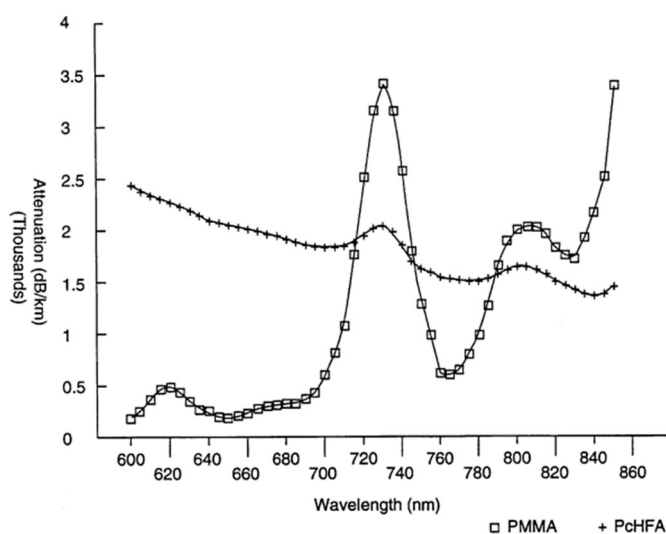


Fig. 4. Attenuation spectrum for plastic optical fibres manufactured with poly (1H, 1H-perfluorocyclohexylmethyl 2-fluoroacrylate) or PchFA, compared to that for PMMA [108]. The optical attenuation was measured using a Bentham Spectrophotometer.

incorporation of 73 wt% fluoroacrylate monomers in the acrylate coating resulted in a refractive index of 1.41798 (vs. 1.4953 at 0 wt%) at 1541 nm and at room temperature while a typical silica cladding used for transmission optical fibres has a refractive index of 1.4439 [35]. A similar observation was made when methyl methacrylate was co-polymerised with different concentrations of trifluoroethyl methacrylate and a commercial fluoroacrylate monomer (Zonyl® TAN by DuPont, USA) [90]. The co-polymers were synthesised by bulk polymerisation and the presence of longer fluorinated side chains was shown to have a more drastic impact on refractive index. This can be of particular importance for very high laser power delivery in order to constrain the leaked power/light from the core to the glass cladding and minimise bend losses. By constraining light within the core and cladding, the coating lifetime can be extended as formation of local “hot spots” [39] at the cladding-coating interface and the subsequent heat-induced degradation of the coating are reduced. Degradation of the coating can lead to increased light absorption and drop in optical power transmittance.

However, achieving a good balance among all aspects of a coating material is imperative. Choi et al. [90] reported a reduction in T_g of fluorinated acrylate polymers with increase in their fluorine content. They attributed this observation to an increase in the free volume of the molecules as a result of the fluorinated side chains. Fluoroacrylate coatings tend to have lower Young's moduli compared to conventional secondary acrylate coatings (typically around 2 orders of magnitude lower) [39,109]. For this reason, fluoroacrylates are better suited as a primary coating in a dual coating system. In addition, fluorine containing coatings are more sensitive to radiation than their fluorine-free counterparts [110,111] which is not favourable for certain applications including medical devices where sterilisation by radiation is often performed.

Apart from the fluoroacrylates, many acrylate oligomer blends and co-polymeric formulations have been developed and characterised over the years, primarily to maximise the operating temperature of optical fibres beyond that of telecom-grade fibres (i.e., 85 °C [15,112]). Wilson et al. [113] compared six secondary acrylate coatings with different formulations based on changes to their colour, weight and tensile strength when exposed to elevated temperatures ($T_{max} = 225$ °C). The coating containing urethane acrylate oligomers and hexanediol diacrylate diluent showed to be the most resistive to change at elevated temperatures. They also reported thermal stability of a series of oligomeric materials including urethane, silicone, melamine and epoxy

acrylates and others like epoxy phenol novalc and bisphenol F epoxy. Among the cured materials tested, silicone modified-urethane acrylates displayed the best heat resistance with $\approx 80\%$ weight retention after 5 days at 225°C . More recently, Stolov et al. [15] compared the performance of a wide selection of OFS (based in Georgia, USA) [114] optical fibres with single- and dual-layer acrylate coatings. The coatings were subcategorised as urethane, non-urethane, silicone- and organic-inorganic hybrid-based acrylates among which the dual-layer silicone acrylate coatings showed the best high temperature performance. Based on a 25 % weight loss criterion for coating failure and a 20-year continuous use assumption [115], this type of coating was predicted to have an upper temperature limit of 130°C . While the presence of silicone made these coatings highly resistive to moisture, the dual-layer coating design imparted less resistivity to bend losses, outperforming single-layer silicone-acrylates. It has also been shown that functionalising epoxies or silsesquioxanes with acrylate reactive groups can expand their operation temperature window up to 140°C [112] but it's unclear how the presence of these moieties impacts other properties such as refractive index, strip force or Young's modulus.

Today, many manufacturers offer optical fibres coated with "high temperature acrylates" with operating temperatures ranging between 150 and 200°C depending on their formulation and length of exposure to high temperatures [116–120]. Many published works report about the performance of high temperature acrylates but often times they fail to disclose the composition of acrylate oligomers utilised [15,28,39], as in many cases the coating composition is proprietary to the manufacturer. This makes drawing conclusions on the most suitable formulations in the family of specialty acrylates for elevated in-service temperatures quite challenging.

4. Polyimides

4.1. Background, chemistry and curing mechanism

Polyimides (PIs) have been utilised in various industrial applications under harsh environments, such as electrical insulators, gas separation membranes, matrix resins for fibre-reinforced composites, and other industries because of their excellent chemical resistance [121,122], high T_g [123], good mechanical properties [121,122], and low dielectric constants [124]. This class of coatings are characterised by an imide repeating unit as shown in Fig. 5a. Since 1960s, various technologies have been developed to prepare PI materials in different forms including films, fibres, coatings, adhesives, membranes, and composite matrices. Polyimides have an upper temperature limit of around 300°C [25,80] and their T_g ranges between 300 and 400°C [121,125,126].

Aromatic PIs are typically synthesised in a two-step process (Fig. 5b) [127,128]. Other (less commonly used) PI polymerisation methods are

listed in recent reviews [122,129]. In the two-step process, polyamic acid (PAA) is first synthesised by polycondensation reaction between dianhydride and diamine monomers in the presence of a polar solvent (e.g., N, N dimethyl acetamide). In this step, which is typically carried out at low temperatures ($< 50^\circ\text{C}$) [123], the carbonyl carbons present in the anhydride monomers undergo nucleophilic attack by the amide groups. The second step is imidization reaction of PAA to form PI which involves gradual heating (from 150°C to 300 – 400°C) [127,128] of PAA solution for solvent evaporation followed by dehydration and ring closure. During the imidization reaction, water is produced as a by-product that can result in polymer chain scission, especially in thicker film casting. To ensure the drying process and PI structure formation during imidization are completed, coating thickness must be kept limited to $\leq 2.0\ \mu\text{m}$ [121]. To create thicker coatings (which in some applications can be beneficial [130]), several deposition cycles are needed which can make the fibre drawing and coating process complex. Addition of acetic anhydride and pyridine (catalyst) to PAA solution can help remove water from the reaction system effectively and prevent molecular weight reduction [127]. Another drawback to the use of PAA for PI synthesis is their requirement for low temperature storage ($< -18^\circ\text{C}$) before application which also makes their shipping process complex (typically kept on dry ice [121]). Storing PAA at room temperature can reduce their shelf life by a few months to years.

Organosoluble PIs have been shown to overcome some of the shortcomings of conventional PIs synthesised from PAA [23,121,126]. In 2015, Semjonov et al. [121] coated optical fibres with an organo-soluble polyimide solution. A co-polyimide compound (containing 6F-dianhydride, 6F-diamine and aniline fluorene monomers) was first synthesised via a one-step high-temperature polycondensation process. This route allows one to forgo the conventional PAA formation step. The polyimide solution was then prepared by dissolving the co-polyimide in freshly distilled cyclohexanone. Once optical fibres were coated with this polyimide solution, they were heated to 350°C in a vertical tube furnace forming a $3.0\ \mu\text{m}$ coating layer in only one deposition cycle. In addition and in contrast to PAA, polyimide solutions do not require storage at low temperatures [23,121]. Therefore, organosoluble PIs present many advantages over the conventional polyimides and allow for more flexibility for the user.

Thermal curing process for PIs can pose limitation to their application on an industrial scale since most optical fibre drawing towers are designed to accommodate UV-curable coatings. In an interesting study reported in 2016, the heat generated from a high voltage UV lamp (reaching temperatures around 260°C) was successfully employed to thermally cure PAA-coated optical fibres in a fibre draw tower [29]. Nonetheless, the high temperature curing process for polyimides can introduce complications such as shrinkage and health risks due to release of harmful solvents. Examples of UV-curable PIs are scarce in

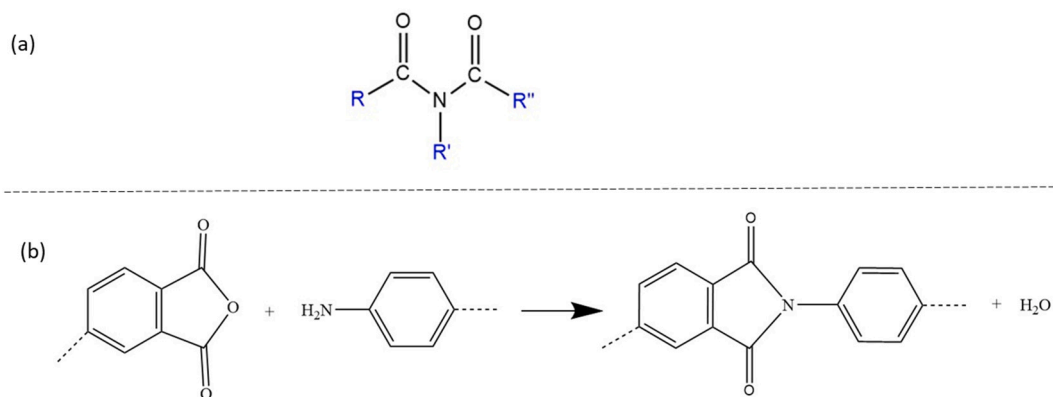


Fig. 5. (a) Imide functional group present in polyimides, (b) Synthesis of polyimides using the conventional two-step reaction. In the first step anhydride and aniline derivative react to form PAA and in the second step PAA undergoes imidization at elevated temperatures to form polyimide and water.

literature [107,131]. Scientists from NASA Lewis Research centre were the first group to synthesise PIs using UV radiation rather than heat. Authors proposed (and M. Meador later patented [132]) a Diels-Alder trapping method of photochemically generated and highly reactive diene intermediates to synthesise PIs [133]. More research was conducted since then to improve the physical properties of the PIs synthesised using this method [134,135]. In a different approach, Liu et al. incorporated glycidyl methacrylate monomers to a PI solution forming a polyimide resin with double bond end groups [131]. By adding a reactive diluent and a photoinitiator, they were able to crosslink $\approx 20\ \mu\text{m}$ thick films of this resin with $200\ \text{mJ}/\text{cm}^2$ dose of UV radiation. The resultant crosslinked PI films showed comparable thermal properties to that of the benchmark formulation (without the acrylate monomers). Despite these efforts, to the best of our knowledge, no UV-curable polyimides have been introduced to the market to date.

4.2. Key properties and limitations

Properties of PIs can vary depending on their chemical structure, functional groups present, molecular weight and crystallinity [136]. Generally, the aromatic chemical structure of PI molecules and the large intermolecular interactions are responsible for their thermal and chemical stability while their flexible molecular links and amorphous structure contribute to their mechanical strength. The type of PI monomers and the PI end groups can influence the final properties of the coating. The diamine region of a PI molecule is presumed the region with greatest electron density and thus, a likely point of oxidation [136]. It is for this reason that diamine regions have higher impact on the stability of the polyimide than the dianhydride region. An electron-rich diamine is less oxidatively stable than an electron-deficient diamine [137]. Thus, electron deficient monomers are typically preferable for stability of polyimides, especially in oxidizing environments. Cella [136] summarised some of the most commonly used diamine and dianhydride monomers for PI synthesis. Among the dianhydrides used to synthesise PIs, Hexafluoroisopropylidene diphthalic anhydride or 6FDA (as shown in Fig. 6) is reported to lead to the most heat-resistant PI derivatives. The presence of electron withdrawing perfluoromethyl groups and the non-rigid molecular structure give rise to improved solubility, unusual surface effects and reduction in water and oxygen permeability of 6FDA. Furthermore, anhydride end groups are preferred over amide end groups. However, anhydride groups can undergo degradation at elevated temperatures and thus, monofunctional chain stoppers are typically preferred (e.g., acetylene and biphenylene) [136].

Being chemically inert, nontoxic, resistive to organic solvents and mechanically flexible make PI a suitable candidate for optical fibre or capillary tube coating in medical devices [138]. However, the chemical and thermal stability of PIs go hand-in-hand with difficult processability. Recent research works have been focused on developing PI coatings with enhanced performance and processability. For example, introducing less heat resistive functional groups or polymers into the PI backbone was shown to improve its processability [123,129]. While acrylate coatings can be removed mechanically, chemical stripping

process is recommended for PIs. This particularly is problematic for fibre coupling where coating is required to be stripped from the cladding. Polyimides are resistant to most organic solvents but they can be dissolved in aqueous acids and alkalis due to the slight hydrophilic nature of these polymers [127]. It has been shown that 1 to 2 min immersion in heated sulfuric acid can successfully remove the PI coating [139].

Polyimides possess higher mechanical strength compared to acrylate coatings, typically around 5 GPa based on two-point bend testing [109,121,139]. However, it has been shown that their mechanical strength can deteriorate upon long-term exposure to high temperatures and high humidity [121,139]. PI coatings are susceptible to loss of plasticity at elevated temperatures which can increase the stress exerted onto the silica fibre, increase in microbend losses and signal attenuation in sensors [30,136]. Reinsch and Hennings's work [20] showed reversible attenuation in the Stokes signal of a DTS system during heating and cooling cycles of PI-coated fibres while irreversible attenuation was shown to take place during prolonged heating at temperatures above $300\ ^\circ\text{C}$. Irreversible attenuation was not observed for fibres kept at $300\ ^\circ\text{C}$. Formation of depressions on the coating surface and colour changes were other reported empirical observations when PIs were exposed to temperatures above $300\ ^\circ\text{C}$. Polyimide coatings exhibit intense coloration, ranging from yellow to dark brown, which is believed to be due to the electron withdrawing and electron donating behaviour of their monomers [140]. Incorporation of perfluoro groups [107,125] and careful selection of the anhydride and diamine moieties [140] have been found to mitigate this issue to some extent. For instance, Khalil et al. [125] prepared different PI blends containing hexafluoroisopropylidene group ($-\text{C}(\text{CF}_3)_2-$). Varying composition of the blends and the overall fluorine content led to significant impact on the transparency and refractive index of these coatings. They achieved the lowest refractive index of 1.5836 for a PI formulation derived from 6FDA and PDA (*p*-phenylenediamine) containing 20.86 wt% fluorine. Wang et al. [107] demonstrated that a decrease in the crosslinking density of fluorinated polyimides can lower the refractive index of this coating (from 1.5866 to 1.5911 at $1550\ \text{nm}$). They added that other factors such as chain flexibility and linearity, geometry of the molecule, polarizability, and orientation of the bonds in the polyimide backbone can also influence refractive index.

Furthermore, high density cabling of PI-coated optical fibres may result in increased attenuation due to the low lateral pressure resistance of this coating [80]. Exposure to water can also increase optical attenuation levels [25]. Use of water-resistant polyimides or use of multilayer systems with polyimide as the primary coating (with lower elastic modulus) has been suggested to reduce the impact from water diffusion on mechanical and optical performance of polyimide coatings [25,141]. PIs can also undergo hydrogen permeation which can impact signal attenuation at certain wavelengths [26]. To overcome hydrogen permeation, a thin layer of carbon can be coated by the fibre manufacturer as a barrier for water and hydrogen [20,31]. However, the effectiveness of this coating can wear off over time especially when used at high temperatures [20]. Laarossi et al. [31] compared the performance of a polyimide-carbon coated fibre (Fibercore GIMMSC(50/125) CP) with that of metal-coated fibres (Cu, Al, Au) in a DTS system intended for long-term high temperature measurements in industrial environments. Their experimental results suggest that a hermetically sealed polyimide-carbon coated fibres can present the most reliable performance for high temperature DTS industrial applications.

Polyimides are commonly used in optical fibre sensors for humidity and temperature sensing [130,142,143]. In particular, fibre Bragg grating (FBG) sensors take advantage of the hygroscopic nature of the polyimide resin coating to carry out humidity measurements [144]. Polyimide coatings undergo linear volume swelling changes with respect to environmental humidity. Wang et al. [144] designed a $\approx 35\ \mu\text{m}$ thick polyimide-coated FBG to measure relative humidity and moisture in industrial oil samples. After fibre core grating inscription, cladding was dip coated with polyimide followed by a heat treatment to

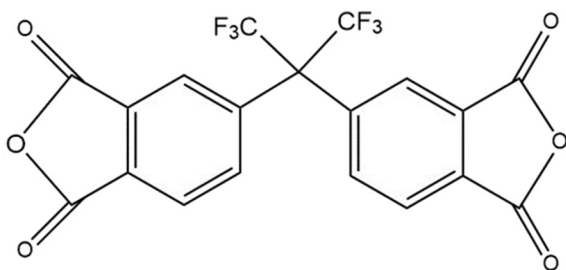


Fig. 6. Chemical structure of Hexafluoroisopropylidene diphthalic anhydride (6FDA), a commonly used anhydride monomer for PI synthesis.

help with cladding-coating adhesion. To achieve their desired coating thickness, this process was repeated several times. The designed sensor by Wang et al. showed high sensitivity with an ability to detect low density moisture levels in the oil samples. In addition, the radiation hardness capability of polyimide-coated FBG sensors [145] indicates the future exploitation potential of polyimide-based sensors in Nuclear research.

Currently, polyimide-coated optical fibres are offered by many manufacturers (for example Thorlabs [146], iXblue [147], Fibercore™ [148], and Molex [149]) for use in different sensors, data communication and medical devices. However, PAAs or organosoluble PIs are not as commonly available on the market. HD Microsystems™ offers a limited range of thermally curable PAA solutions whose specifications are listed in Table 1.

5. Silicone coatings

5.1. Background, chemistry and curing mechanism

Organic chemist J. F. Hyde [150] at Corning Glass was the first to run research to commercialise silicones in the 1930s, which was further developed by F. S. Kipping in the 1940s who named the material “silicones” due to their physical properties causing “sticky messes” [151]. Meanwhile, Rochow and Müller had developed an alternative synthesis method applicable on an industrial scale, now known as the Rochow-Müller process, or Direct Synthesis [152]. Using the Direct Synthesis process, Corning went on to produce a range of silicone products from tyre release sprays and baked resin coatings to extruded silicone parts and non-stick coatings [153]. As a material family, silicones have been a staple for many industries, including leather treatment with Syl-Flex®

[154], sealants and greases [155] and as thermal interfaces [156], such as those in microprocessors. Silicone was even used as the sole material for the Apollo 11 astronauts' boots [157]. As an optical fibre coating, silicone was used in the first successful field trial of a 0.85 µm optical fibre transmission system in Japan in 1978, over a distance of 20 km [158].

Silicones are comprised of an oxygen-silicon-oxygen repeating backbone, with the remaining two silicon bonds connected to functional groups to give the general formula of $\text{O} - (\text{SiR}_2) - \text{O}$, as illustrated in Fig. 7. The physical and chemical properties of the silicone compound can be modulated by changing the functional groups present (typically, an alkyl), allowing for materials from fluid lubricants to hard resins [159]. Being composed primarily of silicon, the thermal properties of silicone-based coatings are generally favourable for applications at elevated temperatures.

The Direct Process, first conducted by Rochow in 1940, consists of passing gaseous methyl chloride over a silicon/copper catalyst to produce a mixture of methylchlorosilanes, including liquid dimethyldi-

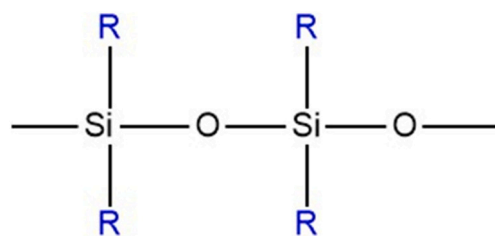


Fig. 7. Molecular structure of silicone.

Table 1

Examples of acrylate, polyimide (PAA and polyimide solution) and silicone coatings for optical fibres and their specifications.

| Coating type | Manufacturer | Coating ID | Curing method | Temperature range | T _g | Tensile strength | Young's modulus | Refractive index |
|---------------------------|------------------|---|---------------|---------------------------|--------------------------|------------------|-----------------|-------------------------|
| Acrylate | Luvantix | ^a PC series [196,203,204] | UV | ^b -20 to 85 °C | 23 to 90 °C | – | 14 to 874 MPa | 1.363 to 1.452 (852 nm) |
| | Luvantix | ^c PC-FB series [205] | UV | – | 43 to 82 °C | – | 55 to 900 MPa | 1.363 to 1.448 (852 nm) |
| | Luvantix | ^d LP- & LS-HT series [196] | UV | >200 °C | From <-100 °C to >300 °C | – | 5 to 250 MPa | 1.410 to 1.436 (589 nm) |
| | Herkula | UltraCoat HT [206] | UV | – | 60 °C | 25 MPa | – | 1.489 |
| | AMS Technologies | ^e LRI-18204 [207] | UV | – | 18 °C | – | 13 MPa | 1.375 (589 nm) |
| | AMS Technologies | ^e LRI-18114 [207] | UV | – | 94 °C | – | 800 MPa | 1.400 (589 nm) |
| | Sartomer | ^f CN2600 series [208] | UV | – | – | – | – | 1.572 to 1.576 |
| | Sartomer | ^g CN4000 series [208] | UV | – | – | – | – | 1.353 |
| | DSM | DeSolite® DP1032 [209] | UV | Up to 85 °C | -44 °C | 0.6 MPa | – | 1.496 |
| | DSM | DeSolite® DF0009 [210] | UV | Up to 85 °C | 2 °C | 23 MPa | 700 MPa | 1.54 |
| | DSM | DeSolite® DF0016 [211] | UV | Up to 85 °C | – | 3 MPa | 10 MPa | 1.37 |
| | Mitsui Chemicals | ECRIOS™ series [212] (e.g., VICT-Bnp and VICT-CZ) | – | Up to 250 °C | 265 to 315 °C | 2.8 to 5.1 GPa | – | 1.64 to 1.67 |
| Polyimide precursor (PAA) | HD Microsystems | PI2500 Series [198] | Heat (300 °C) | – | >320 °C | 128.5 MPa | 2.4 GPa | 1.7 |
| | HD Microsystems | PI5878G [199] | Heat (350 °C) | – | >400 °C | 260 MPa | 2.3 GPa | 1.78 |
| | Microsystems | | | | | | | |
| Silicone | Dow Chemical | SYLGARD™ 184 [109,164] | RT/Heat | -45 to 200 °C | 124 °C | 6.7 MPa | 4.9 MPa | 1.4118 (589 nm) |
| | Dow Chemical | OPTIGARD™ Q3-6696 [213] | UV | -40 to 150 °C | – | – | 0.96 MPa | 1.41 (632 nm) |
| | Luvantix | ^h PC380HT [214] | UV | 150 °C | <-40 °C | – | – | 1.38 (852 nm) |
| | Luvantix | ^h LP-UG series [196] | UV | – | -99 to -35 °C | – | 2.6 to 5.8 MPa | 1.412 to 1.472 (852 nm) |

^a Fluoroacrylate-based.

^b Can be exposed to 150 °C for a short period of time.

^c Low water sorption.

^d Silicone acrylate-based.

^e Acrylate Adhesive.

^f Epoxy acrylate-based.

^g Fluorinated PDMS.

^h PDMS-based.

chlorosilane [160], which is the most common precursor to produce silicones [152]. Chlorosilanes from the Direct Process can react with water in a hydrolysis process to form hydrochloric acid and siloxanediol ($(\text{CH}_3)_2\text{Si}(\text{OH})_2$) which can subsequently be dehydrated to form silanol ($\text{HO}(\text{Si}(\text{CH}_3)_2\text{O})_n\text{H}$) and cyclomethicone ($\text{C}_{10}\text{H}_{30}\text{O}_5\text{Si}_5$) [161]. The processing of silanol, or the hydrated siloxanediol, will depend on the required end-product and the functional group(s) (substituting CH_3 for another ligand) required. These functional groups can be simple alkyl groups (methyl, ethyl, propyl, etc.), or in some cases aromatic substitutions [162] having the effect of increased water uptake and refractive index [163]. Polydimethylsiloxane (PDMS, where $\text{R} = \text{CH}_3$) is often used as a coating material when mixed with a cross-linking agent [109], for example by Dow Chemical's SYLGARD™ 184 [164], the properties of which can be further tuned by controlling the curing process [165].

PDMS is particularly appealing as a coating material due to the ease with which it can crosslink, its flexibility, elasticity [166] and its high biocompatibility [167–169]. Silicone coatings are typically applied by pulling the bare fibre through a liquid silicone coating die or cup which mixes a siloxane and curing agent and applies a thin layer over the fibre [170]. This is then passed through a curing oven at around 250–500 °C to harden. Alternatively, there are UV-curable silicone coatings such as those utilising a monosulphide cross-linking reaction with alkene functional groups [163]. The UV stimulated reaction also requires an initiator and (to increase strength), a reinforcing agent. There are potential issues with reduced thermal stability when compared to heat-cured silicone coatings theorised to be due to the sulphur containing cross-linking agents. For example, when a UV-curable silicone rubber (OPTIGARD™ X3-6662) was kept at 100 °C for 56 h a $\approx 50\%$ drop in tensile strength was reported [163]. Nonetheless, the fast coating application makes the UV-curable silicones an effective coating for low temperature optical fibre applications.

5.2. Key properties and limitations

The curing mechanism of silicone-based polymers can influence the resultant properties of the polymer, as can variations of the curing parameters. UV-cured silicone [163] coatings may exhibit lower Young's Modulus than heat-cured or thermoset silicones (0.55 to 0.7 MPa compared to 4.9 MPa [109] for UV- and heat-cured silicone, respectively). For applications such as vibration damping [171–173], a lower modulus is desirable. The damping properties can be influenced by the addition of phenyl or borate groups [172,173], allowing for use in the vibration reduction for precision instruments. A polyborosiloxane multilayer coating was found to reduce impact damage (8.31 J reduced to 5.82 J with 10 J impact energy; 18.33 J reduced to 16.53 J at 20 J impact energy) and attenuate vibrations from a 5 V noise excitation source by 61 % on a carbon fibre reinforced polymer laminate [173]. Furthermore, silicone coatings with low elastic modulus act as a cushion against mechanical stresses and microbending, minimising the impact on the attenuation levels [114,174].

The lower abrasion resistance in silicones [114] may lead to requirement for a thicker coating (generally thicker than acrylate coatings [113]) and/or a jacket protection layer for industrial applications. Alternatively, silicone-based coatings may have a secondary coating applied to provide abrasion resistance, or to mitigate its gummy or tacky nature in application [175]. Generally, silicones that are UV-cured also typically exhibit lower tensile strengths (0.4 to 2.5 MPa as compared to 6.7 MPa [176]) and viscosities (2.32 Pa·s compared to 3.5 Pa·s [176]) compared to their thermally cured counterpart.

Thermoset silicones exhibit higher thermal stability enabling upper temperature limits of up to 200 °C [112,114,177], whereas UV-cured silicones have a typical upper temperature limit of 100–150 °C. Leoni Fiber Optics, also known as j-fibre, define the operating range of their silicone coated fused silica fibres between –40 to 180 °C [178], while Dow Chemicals rate their Sylgard™ 184 silicone elastomer, which has

been explored as an optical fibre coating [179], up to 200 °C [164]. Thermal degradation of silicone-based coatings initiates around the organic sites present in the polymeric structure. This is predominantly due to higher bond enthalpy related to Si – O bonds (445 kJ mol^{–1}) in the siloxane backbone in comparison to other chemical bonds such as C – C (348 kJ mol^{–1}) or C – N (308 kJ mol^{–1}) [180] in organic polymers.

Depending on the crosslinking agent used, functional groups present and the curing parameters employed, refractive index of silicone coatings can also vary greatly [181,182]. For example, PDMS has a refractive index of 1.41 [166,182,183] while PDMDPS (Polydimethyl-diphenylsiloxane) has a refractive index of 1.43 (when $\lambda = 589$ nm) [184]. The refractive index of PDMS has been found to decrease with increasing temperature, from 1.4085 to 1.3907 at 20 and 60 °C, respectively [185]. Silicone-based coatings from Shin-Etsu reportedly exhibit refractive indices of 1.49 to 1.52 [186], and Dow Chemical's SYLGARD 184 reportedly exhibits a refractive index of 1.4118 (when $\lambda = 589$ nm) [164], although this was found to be subject to the curing temperature where an increased temperature resulted in a higher index value [187].

Silicone coatings can be utilised in a wide-range of harsh environments as they offer good bio-compatibility and high resistivity against water as well as strong alkalis and acids [188,189], making them suitable for biomedical applications such as in implants [190,191], surgical tool coatings [192] and drug delivery devices [193]. Parylene/silicone-coated devices have been developed for bio-implantable optoelectronic devices [190] where the elasticity and chemical durability of the coating can offer mechanical protection to soft devices with a barrier resistant to saline. Their low modulus makes silicones suitable as diaphragm for gas pressure sensors [194] or in hydroacoustic sensors [195]. Silicone coatings may also be used in volatile organic compound gas sensors, as part of an FBG system, utilising their high permeability and porosity [166].

With proper fibre design, silicones can provide a range of useful properties to the overall structure that can enable deployment into new fields and areas of interest. Their relatively low refractive index and flexibility can make them excellent primary coatings in systems where microbending, impact or vibrations are a concern. They can provide reliable chemical durability and remain flexible below freezing temperatures, and stable at steam temperatures, making them viable in applications that require sterilization, such as medical components. Although they offer little abrasion resistance, and their tensile strengths are not typically high, silicone and siloxane coatings are viable, often ideal coatings where these properties are not critical, and the advantages of these systems can be realised.

6. Comparative summary and market overview

A key element affecting the service life and performance of optical fibres in different industrial environments is the stability of their coating layer(s) under the in-service conditions. The extent of optical fibre applications today has led to the development of a broad range of coating materials tailored to meet the application requirements. Table 1 presents examples of acrylates, PAAs and silicone-based coatings and adhesive materials available on the market for optical fibres and some of their properties as reported by manufacturer/distributor. As is reflected in this Table, a diverse range of UV-curable acrylates are supplied by a number of manufacturers. This is owed to the chemical versatility of acrylates enabling fine-tuning of their physiochemical properties. Faster fibre draw and improved water resistivity were the key motivations for the introduction of UV-curable acrylates as coating material for optical fibres in late 1970s replacing silicone rubbers [10,64,67]. Single layer (epoxy) acrylates evolved to dual-layer systems in 1980s to help reduce bend losses and improve attenuation levels [68,69]. In dual-layer coating systems, the primary coating acts like a cushion, damping mechanical stresses while being protected by the secondary coating from abrasion, moisture, and other environmental factors. For this reason, the

secondary coating is expected to have a higher Young's modulus and T_g compared to the primary coating [15,108]. Most conventional acrylates have an upper temperature limit of 85 °C and prolonged aging of these acrylates to extreme humidity [15] and high temperatures [80] lead to degradation and chain scission across the acrylate backbone. These led to commercialisation of more advanced acrylates in the 90s [86]. Fluorinated acrylates were one of the earliest examples of specialty acrylates that offered improved water resistivity as well as enhanced chemical and thermal stability compared to the conventional acrylates. The small dipole moment of the C–F bonds results in low surface tension (better ability to coat the fibre surface) and refractive index (desirable for some applications) [91,98,99]. Presence of these energetic bonds can also bring down attenuation levels at certain wavelengths, particularly in the nIR region [106,107]. However, fluoroacrylates have been shown to be more sensitive to radiation [110,111] (limiting their application in fields such as biomedicine) and lower Young's modulus [108] compared to conventional secondary coatings (making them more suitable as a primary coating in a dual-layer system).

Depending on the acrylate oligomers used (their precursor and molecular weight) properties such as viscosity, curing rate, glass adhesion, Young's modulus and T_g can be tuned [6,13,70–72]. Many acrylate coatings have been developed over the years using different oligomeric blends and polymer chain modification with various functional groups. Silicone acrylates are another great example of specialty acrylates that offer enhanced water resistivity [15], thermal stability [15], and UV transparency [84] (desirable for Bragg grating inscription). For instance, the LS-HT range [196] manufactured by Luvantix (see Table 1) offers an upper temperature limit of 200 °C which is exceptionally high for acrylate coatings. This is enabled by the presence of the chemically stable siloxane groups in the polymeric backbone. Similar to fluoroacrylates, silicone acrylates tend to have lower Young's modulus which can necessitate application of a protective secondary coating.

Silicone coatings offer similar mechanical properties to that of conventional acrylates used as primary coating [15] and certain specialty acrylates such as fluoroacrylates. The soft nature of silicone rubbers makes these coatings prone to abrasions yet desirable for sensitive pressure sensing [194,195]. Silicone coatings are also commonly used in the biomedical field due to their biocompatibility and resistivity to strong acids and alkali [188,189]. The tacky nature of these coatings is often mitigated by applying a secondary coating or using a protective jacket or buffer [175]. It is also common to apply silicone coatings with higher thickness compared to acrylates [113]. Both acrylates and silicone coatings can be stripped mechanically (exhibiting strip forces of 2 to 8 N) [15] allowing easy handling during fibre coupling. Between the thermoset silicone rubbers and the UV-curable silicones, a wide range of physiochemical properties can be presented. Generally, heat-cured silicones possess higher mechanical strength (for e.g., higher tensile strength [176]) and higher upper temperature limit (reaching 200 °C) [112,114,177]. This is clearly evident between the heat- and UV-curable Dow Chemical silicone coatings listed in Table 1 (SYLGARD™ 184 vs. OPTIGARD™ Q3-6696).

When it comes to applications where the in-service temperature exceeds 200 °C (such as DTS systems for geothermal wells), PIs are the frontrunner coating material. PIs owe their high T_g (300–400 °C [121,126]) and onset decomposition temperature (>500 °C [197]) to the aromatic molecular structure and the strong intermolecular interactions. Apart from temperature sensors, the linear volume swelling changes of hygroscopic PIs with respect to environmental moisture levels has made polyimides a great fibre coating material for humidity sensors [122]. PIs also offer tensile and 2-point bend strengths at a few orders of magnitude greater than the acrylate and silicone coatings [198,199]. Unlike acrylates and silicones, PIs have much higher refractive index (see Table 1) and are stripped chemically rather than mechanically [200].

Conventionally, PIs are synthesised through imidization of PAA at high temperatures (150–400 °C) which produces water as a by-product.

To ensure water is fully removed during synthesis, coating thickness must be limited to $\leq 2.0 \mu\text{m}$ [121]. In addition, PAA has a low shelf-life at room temperature and must be maintained at low temperatures ($< -18^\circ\text{C}$) which can add cost and complications during shipping and storage. Efforts have been made over the years to address these complexities associated with the use of PAA as precursor (e.g., development of organosoluble PIs [23,121,126], UV-curable PIs [107,131]). In general, PAA and organosoluble PIs are not as commonly available as acrylates and silicones and to the best of our knowledge, no UV-curable PI has been introduced to the market. Nonetheless, their thermal stability at and above 250 °C give polyimides a unique advantage for deployment in high temperature environments. Development and commercialisation of UV-curable polyimides can open doors to new fields of application for these materials as optical fibre coatings [201,202]. There remains the space for a fast-cure, thermally and chemically durable coating on the market that is competitive in cost to help bring the application of optical fibre sensors to new milestones.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

The authors would like to thank the project partners at IS-instruments, University of Southampton, Glass Technology Services, Breedon Cement, and Wienerberger. The present work has received funding from Innovate UK (GRIFFIN, 95372) and Transforming Foundation Industries Network+ (EPSRC grant EP/V026402/1) and the authors acknowledge, with thanks, the funding organisations. N.V. Wheeler also gratefully acknowledges support from a Royal Society University Research Fellowship. For the purpose of open access, the authors have applied a Creative Commons Attribution (CC BY) licence to any Author Accepted Manuscript version arising from this submission.

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