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Durability of polymer-based materials in concrete structures

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Durability of polymer-based materials in concrete structures

Noel P. Mailvaganam

Polymer-based materials are being widely used in the building industry in various forms such as coatings, membranes, adhesives, sealants, etc. As is well known, these materials can be 'tailored' by the formulator to suit various applications. In this paper, the author describes the specific mechanisms of degradation that a polymer based material can be subjected to and the consequent defects. He argues that to assure predictable performance, the designer must have a good knowledge and understanding of the properties of polymers, how the materials will interact with the environment inservice, and a clear description of maintenance procedures and intervals.

The objective of designers, architects and engineers is to design and construct concrete structures with durability appropriate for the intended use. To achieve this aim we need a better appreciation of the durability of the different components and materials used in construction. Thus, an understanding of the process of deterioration of both concrete and other auxiliary materials (such as plastics and resins) under service conditions is vital.

Polymers are a very diverse category of materials both by their chemical nature and their physical properties. In the building industry, polymers are used in coatings, membranes, adhesives, sealants, and a variety of other fixtures. The properties of individual polymer materials are governed by the many factors peculiar to each material and to the thermomechanical treatment it has undergone^{1,2,3}.

The degradation processes of these materials are quite complex as they result from a series of elementary phenomena that are dependent on a variety of factors. These include composition, (nature of the polymers and additives), impurities, and structural defects produced either during the manufacture of the polymer or its compounding into another finished product³. The processing of many polymers occurs at elevated temperatures (180-300°C) and under mechanical stress⁴. These conditions may incorporate some defects that will act as weak sites during the polymer's subsequent service life, modify the expected properties, and ease its deterioration. For example in the processing of polyethylene in the presence of some oxygen traces, carbonyl groups (---C=O) may appear in its backbone; these groups, which are ultra-violet light absorbers, will constitute weak sites in photodegradation processes. *Fig* 1 shows an example of the chemical network modification in the structure that will cause change in colour, embrittlement, crazing, etc. To avoid the production of such defects, as potential sources of deterioration, it is necessary to introduce special stabilisers during processing.

The performance of the installed product is a consequence not only of the specific chemical composition chosen, but also of the care taken in application and the condition under which the cure reaction of the product takes place. There is often less appreciation of how factors such as (*i*) initial temperature of the material, (*ii*) temperature and humidity during cure, and (*iii*) the mass (bulk of material mixed and thickness of the applied material) of the system affect the performance of thermosetting resins. Some examples that show the effect of such factors are:

- severe retardation of some epoxy systems at 0-5°C
- adverse effects of low initial temperatures on the





handling characteristics and surface wetting properties of resins due to marked increase in viscosity

- the effect on cure rate of one-pack polyurethanes, water dispersed epoxies and neoprenes
- the high rate of setting and cracking of material mixed in large quantities and thick layers applied in a single application, respectively.

Degradation mechanisms

The main deterioration agents to be considered for polymers used in buildings are oxygen, water, pollutant gases (SO₂, NO₂) or oxidising agents (especially ozone) other chemicals, heat, light, bacteria and radiation. A number of these agents act in concert producing both synergistic and opposing effects. The degradation caused by these factors can be categorised into the following mechanisms²⁵.

- Thermal degradation
- Photo-degradation (caused by light)
- Chemical degradation
- Bio-degradation (biological degradation)
- Mechanical or mechano-chemical degradation
- Radio-degradation (x-rays, high energy sources in general).

Thermal degradation occurs where the polymer starts to undergo chemical modifications at a relatively elevated temperature. Changes in temperature drastically alter the properties of polymers and other engineering materials. The strength of most materials is reduced with increase in temperature and sudden catastrophic changes may occur



Fig 2 Effect of temperature on material properties⁶

High temperatures may cause polymers to melt or char. Although some engineered polymers like polyamides are quite heat resistant, most polymers are generally suitable only at low temperatures

when they are heated above critical temperatures (glass transition temperature- T_g or melting point)^{4.6}. High temperatures may change the structure of engineering materials or cause polymers to melt or char. Fig 2 shows the effects of increased temperature on some engineering materials. Although some engineered polymers (polyamides)

have high T_g (>250^oC) and are quite heat resistant, most polymers are generally suitable only at low temperatures.

Thermal aging can cause purely physical phenomena (plasticiser migration or change of morphology) or can promote chemical phenomenon like oxidation. The kinetics of thermal aging of a material is a function of temperature that within a limited temperature range follows Arrhenius type laws⁶.

$log \Delta t = A + B/T$

where A and B are constants

It is possible by experimentation at various temperatures to obtain an approximation of the lifetime Δt at a given temperature. However, caution is required in such an approach as it assumes that there is no transition (or morphological change) for the temperature change under consideration.

The chemical processes of heat deterioration of polymers in the presence of oxygen in the air may be divided into several stages⁷.

An initiation stage:

Polymer $R \rightarrow 2R'$ or $RH \rightarrow R' + H'$

(the R-H links are often the most sensitive to thermolysis)

A propagation stage:

 $R' + O_2 \rightarrow RO_2$ and $RO_2' + RH \rightarrow RO_2H + R'$

A termination stage: in which two radicals combine to form an inactive agent.

By creating new radicals, the decomposition of the RO_2H (hydroperoxides) to RO' and OH' induces the acceleration of the oxidation process:

$$RH + OH \rightarrow R' + H_2O$$
 and $RH + RO' \rightarrow ROH$.

Fig 3 shows the acceleration of the oxidation process, after an induction period that corresponds to the accumulated time before the hydroperoxides interact. Often it is difficult to distinguish between thermal and thermo-chemical degradation because polymers are rarely "pure". Traces of catalysts or impurities present in the material might react with the polymer resins if the temperature is sufficiently high.

Photo-degradation involves the physical and chemical modifications produced by irradiation of polymers with ultra-

violet (UV) or visible light. The existence of light absorbing sites (chromophoric- such as unsaturated groups, hydroperoxide groups) in the macromolecules or additives is a prerequisite for initiation of photo-chemical reactions. Absorption of a photon by a molecule brings it into an excited state and induces photo-chemical reactions (dissociation of chemical bond and formation of radicals) at these sites in the molecule. For example, photons react with carbonyl groups by two mechanisms shown below⁶⁷.



The products (hydroperoxides) that result from the initial reactions easily breakdown under the effect of photons.

hv
R-OOH
$$\rightarrow$$
 RO'+OH

Next, the radicals that are formed react with the RH substrate according to the propagation and termination stages described above.

The principal factors in the environment which determine the extent of the photo-chemical degradation in polymers are the spectrum and intensity of light, the ambient temperature and the presence of oxidising agents in the atmosphere. Photo-degradation depends on the nature of the polymer, on the concentration of defects, or unsaturated sites, impurities, and on the quantity of light energy absorbed by the material. The depth of degradation caused by light depends on whether the material is opaque or transparent to UV light, and its permeability to oxygen^{7,8}, Fig 4.

Chromophores can also be used to prevent degradation. In the form of coloured pigments chromophores not only provide aesthetic appeal but also slow down the process of photo-degradation. The presence of the pigment in the polymer provides a physical barrier to the attack on the polymer resin, and its opacity has a considerable effect on the rate of degradation. This is confirmed in practice by the



Fig 3 Oxidation of polymer in air; y index characteristic of oxidation (for example, amount of oxygen or carbonyl groups measured by IR)



Fig 4 Distribution of photochemical degradation versus depth (one face of the material is exposed to UV rays)⁸ (a) Material transparent to UV wavelengths and permeable to oxygen; (b) Material transparent to UV wavelengths and not permeable to oxygen; (c) Material slightly transparent to UV wavelengths

observed longevity of pigmented materials as compared to clear ones. The physical location and exposure to light will also affect the rate of degradation. Site location, design and the use of shade can slow the process down. Design features that reduce the direct exposure such as overhangs or placement of trees can be advantageous.

Thermal and photo-chemical aging are significantly accelerated by the presence of nitrogen dioxide and sulphur dioxide. Ozone has a particularly severe effect on elastomers whose chains contain double bonds. The chemical network modification that results from photo-chemical or thermal aging is the cleavage of chains, linking or the creation of conjugated double bonds. The first two lead to a modification of the mechanical properties, (for example, strength, *Fig* 5); whereas the formation of conjugated double bonds causes a change in the colour of the resin⁴.

The correct selection of materials, additives and formulation of polymer products can also considerably slow down the photo-degradation process. For example the use of efficient UV stabilisers in polymer formulations will extend the life expectancy of the product. These stabilisers act either via scavenging the free radicals generated during the degradation process or by reversible reaction mechanism.

Chemical degradation

Chemical degradation refers to the processes that occur when polymer products are brought into contact with chemicals. Depending on the nature of the chemical, this type of degradation is known as oxidation, acidolysis, hydrolysis, alcoholysis etc. The reactions start spontaneously and are temperature dependent.

Most polymer-based products will absorb water. Whether in the gaseous or liquid state water may be involved in different processes: it induces the breakdown of the molecules

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by hydrolysis, plasticisation, and solubilisation. The consequences depend upon the severity of the exposure and the service demands. Swelling is the predominant effect observed when absorption of water has occurred. The most sensitive materials are polyamides, polyesters, and to a lesser extent polyurethanes¹. Compounding ingredients are the principal factors in water resistance rather than the basic polymer involved. The use of water-soluble compounding ingredients may result in degradation of physical properties. Hydrophilic (water attracting) compounding materials readily absorb water and should therefore be avoided if the amount

of absorbed water is an important consideration. The combined effect of water and mechanical stress induces stress-cracking⁴.

Many polymeric materials such as epoxies, polyesters and neoprenes used in coatings, sealants and adhesives are resistant to most inorganic chemicals except for highly oxidising agents such as hypochlorites, nitric, chromic and sulphuric acids⁵⁷. Mineral

acids, bases and salts generally have a slight effect upon properly compounded products up to concentrations of 20percent solutions. Aromatic solvents with a few exceptions will soften and swell most compositions. Many aliphatic hydro-carbons however are handled satisfactorily. In general polymeric products resist petroleum products such as freon, alcohol, animal fats and oils³.

The deterioration of polymers due to pollutants takes place in the following sequence:

loss of gloss —> minute crazing—> severe crazing and cracking—> leaching—> loss of reinforcement from the structure —> gradual break-up.

The time scale over which these processes occur is dependent on the microstructure of polymer as well as the type and amount of additives. Discolouration of polymer



Fig 5 Variation of impact strength versus time for a rigid PVC

based products is usually the result of complex photochemical reactions and is due to the attack of some strong pollutants such as sulphites (SO₃), nitrites (NO₂), oxygen (O₂) and ozone (O₃)^{48.9}.

Biological degradation

The correct selection of

materials, additives and

formulation of polymer products

can also considerably slow down

the photo-degradation process

Biologically-initiated degradation is related to chemical degradation because breakdown of the molecular structure is caused by enzymatic action⁸. Micro-organisms produce a variety of enzymes capable of reacting with natural and synthetic polymers. The attack is specific with respect to both

the enzyme and polymer and the site of attack. Polymers containing hydrolysable groups in their main chains would be especially prone to microbial attack. However, the majority of synthetic polymers are rather inert to biological attack.

Mechanical degradation

Mechanical degradation generally refers to macroscopic effects brought about by shear forces.

There is a strong interrelationship between the different modes of polymer degradation. Frequently, circumstances prevail that permit the simultaneous occurrence of various modes of degradation^{10,11}. Typical examples are:

- environmental processes, which involve the simultaneous action of ultra-violet light, oxygen and harmful atmospheric emissions; or
- oxidation deterioration of polymers (thermoplastics, elastomers, etc); which is based on the simultaneous action of heat and oxygen.

Defects due to deterioration

Typical defects that result from the deterioration of polymeric materials are discussed below:

Coatings

Chalking of coatings

Chalking is strictly a surface phenomenon in which the paint film powders on the surface. It is due to the exposure of a coating to the actinic rays of the sun and the action of radiation on the organic binder. All of the air borne reactants for example, humidity, oxygen, air pollutants, combine with light to destroy the resin on the surface exposing the loosely bound particles of pigments and fillers.

Amine epoxy or epoxy ester coatings chalk rapidly³². The problem is directly attributable to the phenolic base of the epoxy resin and such coatings should be restricted to interior use. When an epoxy coating is required for use in an exposed area, the chalking phenomenon can be reduced by the application of a clear coating of a non-aromatic based polymer that has been suitably formulated with the appropriate UV stabilisers. Other resins such as acrylics and the newer epoxies and alkyds now have excellent chalk resistant properties^{2,12}

Although chalking of coatings is considered to be unacceptable under most situations, some coatings (white) are developed for specific applications where this property is sought. These applications include situations where maintenance is difficult and where a bright white surface is required. In such situations the coating used provides selfcleaning characteristics through the gradual wearing away of the surface. The coating is formulated using anatase titanium dioxide as the white pigment in place of the stable rutile grade.

Peeling and blistering

Coatings often flake off regardless of quality or primer used. The cause may be due to premature solvent evaporation, improper surface preparation, paint incompatibility, or moisture problems. Moisture movement through the concrete to the surface may push off the paint. Also differences in expansion and contraction between the concrete substrate and the polymer matrix can result in premature deterioration of the polymer. A high modulus paint cannot accommodate the difference in expansion and contraction between it and the concrete when subject to large

changes in temperature. A typical example is the use of a polymeric based seamless floor in a food processing or hospital location. Often in these locations live steam is employed as part of the routine cleaning process. If the thermal properties are not compatible the coating matrix will be subject to considerable stress resulting in cracking, splitting and chipping of the polymer matrix.

One of the most common causes of failure related to adhesion of a coating is blistering. Blisters can be large or small, although, generally they are round, either dry or liquid filled hemispherical projections of the coating, *Fig* 6. The usual cause for blistering is the penetration of moisture through the coating into areas of poor adhesion. This can be caused by: moisture migration from the slab on grade; moisture entrapment due to the application of a non-pervious coating over surface dry concrete where the surface has been prepared using acid etching or water blasting. Other conditions that can cause blisters are incompatibility between the top and base-coats, solvent entrapment and incorrect selection of primer. There are two types of blister:

- (i) those formed between the coating and the substrate, with the coat separating from the substrate, and
- (ii) those formed between coats and where the top coat separates from an undercoat, forming circular blisters¹².

Peeling occurs due to the application of coatings on concrete surfaces containing a layer of laitance (fine powder) due to bleeding and poor surface preparation and multiple re-coating of a surface. In the latter, new paint is applied over sound or partially degraded coating. With loss of properties of the original coating and subsequent build up of coatings considerable stresses can build up both between and within the various layers. When the stresses can no longer be tolerated by the coating, cracking and peeling occurs.

Alligatoring, checking and wrinkling

These conditions are usually caused by: application of the top coat too quickly over the primer coat, thereby entrapping solvent; use of incompatible coating systems; solvents within the top coat that either attack or soften the previous layer.

When changes in temperature occur, the paint film contracts or expands, if the top coat is not elastic it will crack¹².

Checking may be described as small breaks in a coating surface that are formed as the coating ages and becomes harder and more brittle. It is a surface phenomenon and does not penetrate the full depth of the coating. For the most part this is a formulationrelated problem where the fillers and resins have not been combined properly. Alligatoring can also be considered a checking reaction in which the surface of a coating hardens and shrinks faster than the body of

the coating itself. Unlike checking the surface cracks into large segments. Wrinkling is usually associated with coatings that are applied at too great a thickness. Wrinkling in contrast to checking (where shrinkage is the cause of defect formation) is the result of the more rapid expansion of the surface of the coating than the body of the coating during the drying period.

Sealants

Many polymeric materials such

as epoxies, polyesters and

neoprenes used in coatings,

sealants and adhesives are

resistant to most inorganic

chemicals except for highly

oxidising agents such as

hypochlorites, nitric, chromic and

sulphuric acids

Fundamental to the longevity and successful performance of sealants is proper application. Application has two aspects – design and installation. The cyclic strain to which a sealant will be subjected to is dependent on the magnitude of the movement at the joint and the width of the sealant. Thus, an important prerequisite in sealant selection is an estimate of the nature and extent of the anticipated movement and a



Fig 6 Round blisters on floor coating

match of the expected movement on the predetermined joint width to the sealant's movement capability.

As the joint opens and closes, the sealant behaves in a composite elastic and plastic manner. The type of action predominating at any time depends on the shape of the joint, the extent and rate of movement, installation temperature and physical properties of the selected sealant. The movement at the joint is dependent on the temperature range the building element experiences, coefficient of thermal expansion of the concrete, and the length of the building element. These factors are used in the calculation of the minimum joint width required to allow the joint to operate without exceeding the movement capability of the sealant. Other factors that need

to be taken into consideration prior to, and during installation include shape, dimension, and location of the sealant bead, surface preparation (removal of contaminants, use of primers for better bonding), installation temperatures and potential irreversible movements (for example, shrinkage and creep) in the building components^{4,13}.

Installation temperature will significantly influence the degree of strain experienced by the sealant in the joint. A sealant installed at mean temperature (halfway between maximum and minimum values) will

operate within its movement capability, in tension in winter and in compression in summer, Fig 7(a). If the sealant is installed when the building element is at much lower temperature, offering a wider joint, the sealant will experience a greater strain in compression than in tension, Fig 7(b). It is less likely to fail, because the maximum tensile strain it undergoes will be reduced and its adhesion to the surface will be augmented by the predominance of compressive forces. However, failure could occur if the joints were narrow, or the sealant put in place at very low temperatures. Under



Fig 7 Potential effects of temperature conditions at time of sealant application¹⁴

these conditions, high tensile strains could be induced at the sealant surface by excessive extrusion of the sealant from the joint. In addition other adverse effects that result when the sealant is installed under cold weather conditions $\frac{1}{3}$ such as flow and slow cure problems — are important considerations. If the temperature at the time of installation is higher than the average temperature, the sealant will experience an increased strain in tension during winter when the sealant material itself will be somewhat harder and less capable of extension, *Fig* 7(c). The minimum joint width might have to be increased in anticipation of this situation⁴.

A definite geometrical relationship of changing sealant cross-section exists during extension and compression. The

An important prerequisite in sealant selection is an estimate of the nature and extent of the anticipated movement and a match of the expected movement on the predetermined joint width to the sealant's movement capability depth to width proportion referred to as the shape factor determines the joint's efficiency. As the sealant's crosssection adjusts during extension and compression, its internal strains increase with the maximum value occurring in the outer region. The depth to width ratio determines the strain, and by simply reducing the joint's depth, the strain in the sealant bead is significantly reduced, *Fig* 8.

In addition to joint design and mismatch of sealant type/joint requirements, adhesion and elongation properties of the sealant are

adversely affected by (*i*) water immersion, (*ii*) aging which causes a continued cure resulting in higher modulus or migration of plasticisers and volatiles which also result in higher modulus and shrinkage; (*iii*) low temperature which causes an increase of modulus or stiffness of the sealant; UV light; heat; chemical attack.

Water immersion

In general the high performance sealants can be considered to be hydrolytically stable. However, there does seem to be evidence that the weathering of polymers (polysulphides, polyurethanes, and silicones) is best accounted for by slow



Fig 8 Strain on the extreme fibre of sealant for different shape factors

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Fig 9 (left) Sealant prior to weathering; (right) Sealant after weathering (8000 hours) showing cracking

depolymerisation that occurs in the presence of moisture and must therefore be regarded as a hydrolytic breakdown⁷. At atmospheric temperatures and intermittent exposure to moisture such hydrolysis proceeds very slowly. Under immersion conditions, however, a number of commercially available sealants absorb water and swell. This is because all sealants include substantial amounts of filler that readily absorb water. Powders such as stearate-coated calcium carbonate however, determine the degree of water uptake⁴⁷.

Aging

Most sealants continually get harder and stronger with time, resulting in an increased modulus of elasticity. If the sealant modulus increases too much, the cohesive strength becomes greater than the adhesive strength of the sealant substrate bond line. Consequently, the seal at the joint may fail if the substrate is not strong enough to resist being pulled apart with normal sealant movements. In situations where the substrate is strong such as aluminium or steel, the sealant must retain some movement capability consistent with the application to avoid cohesive failure.

The performance of a joint sealant can be enhanced by the use of physical barriers (metal or polymer cap) to protect the joint from physical or chemical attack in locations where it is subjected to intermittent chemical spillage. This technique can also be used to protect the sealant from UV and air pollutants.

Effect of cold temperature

All sealants — polysulphides, polyurethanes, and acrylics – are well known to stiffen in the cold. Some sealants will undergo gradual crystallisation if subjected to very cold temperatures (-40°F/-40°C or below) for long periods¹². The crystallisation is gradual and it generally restricts severely a sealant's ability to elongate and perform.

Effect of heat

Sealants often fail in the heat—particularly those installed in cool temperatures, when the joint is wide. In summer when the joint is closed, the molecules of the sealant relax and reorient. The effect is as if the sealant were cured in the compressed state (compression set). When the joint opens as

Adhesives

Adhesive joint failure may involve cohesive failure in the body of the material or adhesive failure in the interfacial area or a combination of both the mechanisms. Some of the factors affecting the adhesive bond are (*i*) modulus of elasticity; (*ii*) fillers; (*iii*) adhesive thickness; (*iv*) temperature, and (*iv*) interfacial imperfections and (*vi*) pressure^{4,9}.

Modulus of elasticity

Most of the polymers used in adhesive tend to harden as they cure. Therefore, the modulus of the cured adhesive gradually increases as it ages. If the modulus of the cured adhesive in the bond line is high and a significant difference in the coefficient of thermal expansion between the adherents exists, there is a strong likelihood of early joint debonding. Where large differences do exist, it is usually beneficial to use an adhesive of low modulus.

Fillers

The effect of fillers on the durability of adhesives is dependent on the type of fillers used. For example, epoxy adhesives filled with aluminum powder or china clay produce more durable joints than products containing calcium carbonate. The degradation that results when the latter products are subjected to long periods of exposure to moisture can be traced to the greater water uptake by calcium carbonate fillers.

Adhesive thickness

Some studies show that adhesive joints with thicker bond lines had shorter lives when subjected to fatigue^{4.9}. The weakness of thicker joints has been attributed to stresses built into the joints by the contraction of the adhesive on setting or in part due to the change in the rate of straining which occurs with increased thickness, *Fig* 8.

Temperature

Although thermosetting resins in adhesives have no softening point, they still show a change in joint strength at higher temperatures that appears to be independent of any thermal degradation processes. The decrease in strength has been explained by a plastic flow phenomenon and is governed by the glass transition temperature, T_s , of the polymer used.

the weather cools, the sealant takes the full movement in one direction as a large extension force. This causes the sealant to fail in adhesion, *Fig* 7.

UV light

UV light can cause widely varying amount of deterioration in sealants. The symptoms of this deterioration may be chalking or cracking, *Fig* 9. Normally, unless the polymer is a weak one, the rate of chalking is not a factor because of the relatively thick sections used in sealant applications. In general, the effects of temperature on bond strength are the result of stress concentrations and gradients developed with the joint. These stress concentrations are due to many causes, including: differences in thermal coefficients between adhesive and adherents; shrinkage of adhesive in curing; trapped gases or volatiles evolved during bonding; modulus of elasticity and shear strength differences between adhesive and adherents, and differences in thermal conductivity; and operating at very low temperatures (-40°F/-40°C) intensifies stress concentrations because of the magnified differences in the physical and mechanical properties of adhesives and adherents. For example, a low modulus adhesive which can stress-relieve itself at room temperature by deformation will increase its modulus of elasticity at very low temperatures to the degree that stress-relieving is no longer possible.

Interfacial imperfections

Interfacial imperfections can arise through the normal adhesive curing process. An imperfection such as a trapped air bubble in the cured adhesive can be the site for high-localised stress, which can accelerate the debonding effect in service environments, which include water. Also, adhesive shrinkage that accompanies curing is a principal factor in bond failure. Adhesives that cure after wetting the surface of the substrate by solvent evaporation, cooling or chemical polymerisation mechanisms are all candidates for failure^{4,10}.

Pressure

Pressure has a positive effect on the adhesive bondline. It can promote better wetting and spreading of the adhesive on porous substrates and thereby reduce interfacial imperfections like air bubbles or voids, and increase uniformity in the bondline.

Summary

Perhaps the major factor that has been responsible for the extensive use of polymer-based materials in civil engineering is their versatility. They can be 'tailored' by the chemist/ formulator for a wide variety of applications. However, this very versatility demands that the designer, specifier, and user first acknowledge the likelihood of polymer-concrete mismatch and secondly, exercise a clear means of judging materials at the design and selection stage. As with all materials they will lose their functionality with time and exposure. By understanding and being aware of the mechanisms and agents of decay the life expectancy of polymeric materials can be maximised^{9,15}.

To assure predictable performance, the designer must have a good knowledge and understanding of the properties of polymers, how the materials will interact with the environment in-service, and a clear description of maintenance procedures and intervals. Consideration of the following factors, alongwith a good maintenance and repair programme will ensure that polymers will function effectively in the concrete structure¹⁶.

- Knowledge and understanding of the limitations of the products selected and used.
- Proper design of the construction elements.

- Service conditions expected, particularly aggressive agents, temperature fluctuations and wear.
- Surface preparation and application methods and conditions.
- Maintenance programme.

References

- HEWLET, P. C. and HURLEY, S.A. The consequences of polymer-concrete mismatch. Proceedings on the joint symposium on the design life of buildings. organised by ICE, Concrete Society and RIBA, 1984, Thomas Telford, pp. 26-27, 179-196.
- OHAMA, Y. Polymer-based materials for repair and improved durability: Japanese experience. Special Issue on Investigation and Repair of Concrete Structures, ed. Mailvaganam, N. P., 1996, Vol. 10, No. 1, pp. 77-82.
- Epoxies with Concrete. ACI Publication SP 21. 1968. American Concrete Institute, CI, Detroit, Michigan. pp., 5-8, 29-36 and 93-106.
- WAKE, W.C., ed. Synthetic Adhesives and Sealants, John Wiley and Sons, pp. 106-108, 1987.
- MAILVAGANAM, N.P., ed. Repair and Protection of Concrete Structures, CRC Press, Florida, USA, 1992. pp 31-42.
- 6. ASKILAND, D.R. The Science and Engineering of materials, Brooks/Cole 1984.
- EURIN, P. Degradation processes of organic building materials: A short review and some proposals for research. *Durability of Building Materials*, 1982, Vol. 1, No. 2 pp. 161-168.
- JELLINEK, H. H. G. Aspects of Degradation and Stabilization of Polymers, Elsvier, Amsterdam, pp 78-84, 1978.
- SASSE H.R., ed. Adhesion between polymers and concrete. Proceedings of the RILEM International Symposium, Paris, September 16-19, 1986, pp. 144-151 and 230-244.
- HEWLET, P. C. Assessment and evaluation of polymer-based repair materials Concrete International, March 1993, pp. 39-4.
- SCHUPACK, M. Divorces and ruptured relations between epoxies and concrete, Concrete Construction, October 1980, pp. 735-738.
- ALFRED, R., ALFRED, H. and GUSTAV, P. Experiences on barrier layer on the surface of concrete. Proceedings of the RILEM Seminar on Durability of Concrete Structures under Normal Outdoor Exposure. March 26-29, 1984, Hanover, pp. 116-125.
- KINLOCH, A.J., ed. Durability of Structural Adhesives. Applied Science Publications pp. 108-112, 1983.
- 14. SCHUTZ, R.J. Precast Concrete Institute, 4.2.1, 1996
- CUSSON, D. and MAILVAGANAM. N. P. Durability of repair materials. Concrete International, March 1996, pp. 35-38.
- PLUM, D. Materials What to specify? Construction Maintenance & Repair, July/ August 1991, pp. 3-7.



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