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Irradiation Effects on Organic Materials

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Please note

Some of the effects of irradiation on organic building materials were referred to in **CBD 117**. The present Digest is intended to discuss these processes in more detail. First, however, some attention should be given to irradiation and radiation. The latter is an electromagnetic form of energy which, unlike heat and sound, can be transmitted across space as well as through some materials. Irradiation occurs when a material is subjected to radiation; it is measured as the amount of energy incident upon a surface of given area in a given time.

Electromagnetic radiation is in wave form and may be described by the wavelength or the frequency of vibration. Frequency is more fundamental but wavelength is more easily determined and has been more commonly used. As wavelength decreases frequency increases.

The complete range of electromagnetic radiation is divided into regions according to properties and wavelengths, as shown in Table 1. The shorter wavelengths are measured in smaller units, Ångströms ($1\text{Å} = 10^{-10}$); as the wavelength increases, so does the unit. As with most classifications, the lines between regions are not sharp and one type gradually merges into the next. This is true even with visible light, where the actual limits vary with the individual and his age, although the stated range is 400 to 770 nm. Some people can see down to 320, but the sensitivity is very low (at 350 it is only about 1 per cent of that at 400). Hence, radiation below 400 is called ultraviolet (UV) down to 10 nm (100 Å).

Table I. Divisions of the Electromagnetic Spectrum

Name	Wavelength Range		
Gamma Rays	0.01	1	Å
X-Rays	1	100	Å
Ultraviolet			
Extreme UV	10	100	nm
Far UV	100	200	nm
Middle UV	200	300	nm
Near UV	300	400	nm
Visible Light	400	770	nm

Infrared			
Near IR	770	2500	nm
Middle IR	2.5	30	μ
Far IR	30	300	μ
Hertzian Waves			
Microwave	0.3	100	mm
Radio and Television	0.1	1000	m

In the environment normal to most buildings the kind of radiant energy having the greatest effect on organic materials is that which maintains life on earth -- solar radiation. Until man starts building on the moon, he will be concerned with solar radiation as it is received at the earth's surface. Figure 1 compares the distribution of energy in the solar spectrum above the earth's atmosphere with that at sea level, with the sun directly overhead at noon.
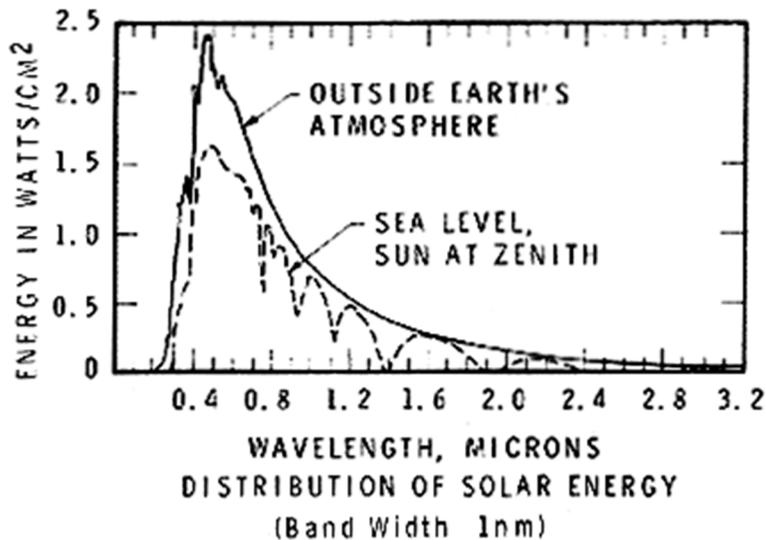
Figure 1. Distribution of solar energy (Band width 1 nm)

Solar radiation is considerably modified by the atmosphere even at the zenith. The peak in energy has been shifted from the blue to the yellow-green in the visible region, and infrared radiation (IR) is reduced owing to absorption by water vapour and oxygen. Finally, and of greatest importance, only near-UV is received at ground level although the sun emits down to 200 nm. This UV absorption is caused by ozone in the upper atmosphere. Reduction in energy is still greater when the sun, because of time of day or year or latitude, is not at the zenith. At lower angles, radiation has to travel farther through air and consequently more energy is absorbed. In addition, at lower sun angles the shorter wavelengths are scattered more, so that only about half the UV comes in a straight line from the sun.

The importance of absorption of middle UV is related to one of the characteristics of radiation: the shorter the wavelength, the higher the energy content. As discussed in **CBD 117**, polymers used in organic building materials are composed of long-chained molecules with carbon-to-carbon backbones. The molecules may be bound to each other by secondary forces and entanglement alone or, depending upon the type of polymer, by chemical bonds as well. Because the primary bonds are chemical and their strength depends upon the elements involved, they can be broken by sources of energy that exceed the attractive forces between the atoms, thus disrupting the molecules. In radiation, this level of energy is reached for the carbon-carbon bond at approximately 350 nm, which is well within the range of solar radiation received at sea level.

Fortunately, the proportion of shorter radiation is small. At noon in the summer UV provides 5 to 7 per cent of the total energy, and biologically active UV (less than 320 nm) about 1 per

cent. These proportions decrease before and after noon and in winter because of the geometric effects mentioned above. For example, at 40° north latitude the four winter months November to February supply only about one-ninth of the biological UV provided by the months from May to August. In addition, clouds and smoke reduce total radiation and the intensity of UV. If it were not for these various factors. no organic polymer (including man) would have any exterior durability.

Action of Radiation

When a molecule absorbs radiation it is raised to an excited state, usually at one particular atom. It may return to its unexcited or ground state by dissipating the energy by re-radiation of fluorescence, phosphorescence or heat. In such a case the molecule is unaffected. This is what happens with longer-wave radiation which is turned into heat. If radiation contains sufficient energy. however, it may cause a chemical reaction at the excited atom and this frequently leads to degradation of the material.

Before either of these courses can be followed it is necessary for radiation to be absorbed. Just because a material is irradiated it does not necessarily mean that absorption occurs. Certain molecular arrangements absorb certain bands of radiation. and this is why some materials are red and others are blue. If none of the groups that absorb visible light is present, the material is colourless (or white if the light is reflected). This transparency or lack of absorption can also occur at wavelengths other than those in the visible region. Thus some materials may be transparent to UV but absorb visible or IR and vice versa. The reason why no IR above 2.4μm is received from the sun at the earth's surface is that water absorbs strongly in this region, although it is transparent to visible and near-UV light. Similarly, ordinary window glass is opaque to that part of the UV that causes sunburn.

When a material is transparent to a particular wavelength, it means that that radiation passes through the material without effect. Consequently. if a material transmits all the UV down to 300 nm, it will not be degraded by the sun. Acrylics such as polymethylmethacrylate (PMMA) do not absorb until well down into the middle UV and this is one reason for their excellent exterior durability. Polystyrene, however, is made from aromatic groups, which absorb at the lower end of the near-UV. As a result, polystyrene is affected by exterior exposure, usually turning yellow and losing some of its mechanical properties.

It is not sufficient for the basic polymer to be transparent. Initiators used to start the reaction must be removed after polymerization or not absorb UV. Impurities that cause absorption must also be absent, but this is difficult to accomplish in large-scale production at elevated temperatures. Small quantities of absorbers can have an effect out of proportion to their amount because absorption frequently produces chemical groups that absorb additional UV. The reaction therefore becomes faster and faster with time.

In some circumstances transparency to UV is a benefit to materials used in bulk, but it can also be a liability if the substrate to which a clear coating is applied is affected by radiation. Hence, clear acrylics do not perform well on exterior wood because the top layer of wood is degraded and the coating, left without support, peels off. Alkyds and urethanes act in a similar manner although they absorb somewhat higher into the UV.

Effect on Chemical Constitution

Because the UV portion of radiation contains the most energy, it causes the greatest damage to organic materials. Chemical degradation attributable to it can take two paths. With some materials the energy starts a process the reverse of the polymerization reaction that originally produced the large molecules. The polymer may be broken in isolated locations - called chain scission - or it may completely revert to small molecules. The latter is the so-called "unzipping" of the polymer that fortunately occurs very slowly when radiation is the only factor. In the second process, the smaller molecules produced by chain scission or reactive sites on large molecules react with other chains. This results in more cross-linking than was originally present so that the material becomes harder and more brittle.

Chemical changes of a less destructive, though still undesirable nature, occur if UV alters a resin's internal structures to those that absorb blue visible light. The reflected light then appears yellow, and this is generally undesirable. Another visual defect can be caused by UV, even though the polymer itself may be resistant, if the material is coloured and the colorant, many of which are organic, is not. Fading, which is usually not acceptable commercially, then occurs.

Only UV possesses sufficient energy to break the primary bonds, and the only chemical effect of visible and infrared radiation is to speed up the rate of reactions that may be occurring from other causes. The quantity of heat in solar radiation is not sufficient to raise the temperature to where chemical bonds can be broken thermally.

Effect on Physical Properties

Radiation-induced changes in the physical structure of organic materials result from the chemical reactions that have taken place. Because large molecules are required for a material to have the desired physical characteristics, the material soon loses these properties if scission reduces the molecular weight too much. When radiation causes marked depolymerization, catastrophic failure occurs. For example, polymethylstyrene, which should be less brittle than polystyrene, has not been of commercial importance because it slowly reverts to monomer when irradiated by UV of 280 nm at room temperature. At 115°C the effect of UV is 70 times greater than that at 25°C, but without UV there is no degradation at all at the higher temperature. This illustrates the synergism common to degradation processes.

If cross-linking occurs, either from chain scission or at active sites, the material is affected because of the relation between cross-link density and physical properties. If some flexibility is required for the building material to perform its function, the additional hardness causes cracking. Thus, some coatings become less extensible and crack when they can no longer accommodate movements of the substrate. If sealants cross-link too much they either crack or lose adhesion at the interface.

In some cases initial irradiation products are coloured and absorb subsequent UV light, thus preventing deeper penetration of the radiation. As only the outer layer becomes crosslinked, cracking is restricted to that region. When the material has a thick cross-section, as do many structural plastics, the process results in surface cracking or crazing, depending upon the depth of the cracks. Polystyrene exhibits this type of behaviour upon exterior exposure. With coatings, which are relatively thin, the cracking may be deep enough to penetrate to the substrate. Pigmentation, however, may restrict excess cross-linking to a very thin layer, and if the cracks are microscopic they will result in chalking from the gradual erosion of this layer. The cross-linking process is more common in the degradation of organic building materials resulting from solar UV than is the depolymerization reaction.

Summary

What is radiation; which part of it is involved in durability problems; how does it affect the organic materials used in and on buildings? Ultraviolet light between 350 and 300 nm is shown to be the most damaging radiation. It acts by changing the chemical structure of the polymers used in organic building materials, consequently affecting their physical properties. *Fortunately*, the intensity of destructive UV is a small part of the total solar radiation and is reduced as the angle of the sun decreases and by clouds and smoke. *Unfortunately*, enough UV is received on the surfaces of buildings to cause degradation of materials, particularly when it acts in conjunction with oxygen, water, heat or a combination of these elements.