11 DEGRADATION OF POLYMERS

Although polymers are reasonably stable but they undergo degradation especially on exposure to oxygen, moisture, ozone, radiation, stress and heat. These agents either lead to the breakdown of chemical structure of polymers resulting in a loss in strength and toughness or there may be some structural modifications like cross linking (It may lead to brittleness, hardness and changes in solubility), Development of chromophoric groups (It may lead to colour formation) ; and Development of polar groups (It may lead to deterioration in electrical insulation properties). Such structural changes are the consequence of following chemical reactions : oxidation, ozone attack, ultra-violet attack, dehydrochlorination etc.

Oxidation. It is caused by contact with oxidising agents, prolonged application of excessive heat etc. It results in embrittlement and stress cracking, deterioration in electrical insulation properties and loss of clarity. It affects most thermoplastics to varying degrees, in particular PE, PP, PVC, Nylons and unsaturated polymers like rubbers etc.

dation can be prevented by adding UV-deactivators.

Weathering. It occurs as a result of the combined effects of absorption of water and exposure to UV-radiation. Water absorption can have a plasticizing effect on plastics and it increases flexibility. It also reduces dimensional stability of moulded articles. Ultimately, on elimination of water, plastics undergo embrittlement. UV-radiations causes chain-scission and hence deterioration of physical properties. A loss of clarity or colour (or both) may also occur.

Examples of polymer which are susceptible to weathering are : cellulose derivatives, PE, PVC, nylons etc.

Environmental Stress Cracking (ESC)

Some polymers (like PE) when exposed to a mechanical stress in active environments (like alcohols, liquid hydrocarbons, metallic soaps etc) underdo ESC. Fracture (brittle cracking) of the sample occurs at stresses much lower than in the absence of the environments. This might be due to reduction of molecular cohesion to the greatest extent by these active liquids. The stresses may be residual (*i.e.*, Internal) or externally applied.

Mechanism of ESC : It proceeds by the penetration of the molecules of active liquid at surface defects, followed by reduction of molecular cohesion by modification of surface energy and then finally brittle cracking results.

Thermal degradation

It causes adverse changes in mechanical and electrical properties of PVC, when PVC is heated to above 150° C in the presence of oxygen. The dehydrochlorination process results in the formation of a conjugated polyene.

$$-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}- \xrightarrow[-HCl]{\text{Dehydrochlorination}} -CH=CH-CH=CH-CH=CH-$$

Polyvinyl chloride — Conjugated Polyene

The polymer consequently changes its colour in the sequence :

Water white → Pale yellow → Orange → Brown → Black

With increase in extent of thermal degradation

liberated HCl accelerates further decomposition. Thus for retarding the degradation of PVC, *stabilizers* have to be added which react with the liberated HCl