3.2. Physical and chemical processes leading to deterioration of original properties of plastics

Plastics in museums and depositaries display different degree of stability that depends on their chemical composition and the presence of additives. It is affected by:

- Heat
- Oxygen
- Light of wavelength >300 nm
- High energy radiation
- Mechanical stress
- Biological attack
- Hydrolysis associated with relative humidity
- Contacting liquids
- Removal of additives
- Initial molar mass and its distribution

The methodology of evaluation of the extent of degradation of any plastic in museums and exhibitions is very closely linked with its identification (Chapter 1), with the possibility to undertake micro-chemical tests as well as physical measurements. Generally, any method of identification when repeated several times within the time lags may bring the comparative information on the development of plastics degradation. The smell, shape, transparency and/or colour, blooming of low molar mass products of degradation or additives on the material surface and the staining, brittleness, the change in adhesion of water, structure and state of the surface, crazings and/or crackings observable in material, material flaws, warping, scratching, wear, haptic and tactile properties, tearing and peeling are some of the artifact properties which can provide the identification clue to the material quality and its dating. This may be accompanied by the extent of biological attack, loss of object

parts, state of the dust and grease adhesion to the surface. All data from the object's history and design are also of importance because some materials were used only for several applications and within a certain period after which they were replaced by other material. One, however, must be aware of the fact that identification based on physico-chemical and chemical analysis is the only first step which is necessary in the determination of the extent of degradation. Its importance consists in the possibility that it is a guide in alternatives of subsequent stabilisation and consolidation.

Physical degradation involves environmental stress cracking and plasticiser and/or other additive migration and loss.

Chemical reactions involved in degradation of plastics include the typical oxidation and hydrolysis paths. Oxidation may occur under various modes as e.g. the stripping out of side groups which is typical for the cellulose esters (cellulose nitrate and cellulose acetate), and plasticised poly(vinyl chloride) that emit acidic degradation products while leaving the unsaturated main chain which becomes considerably more reactive towards further oxidation. If not removed, these acids catalyse subsequent reactions and eventually cause serious crazing and total destruction of the object. Artefacts containing polyurethanes degrade predominantly hydrolytically (polyester urethanes) or as a light induced oxidation (polyether urethanes).

Chemical processes related to the worsening of polymer properties may lead to both the reduction of average molar mass due to the scission of bonds in the macromolecular chain or to the increase of the molar mass due to the cross-linking while polymer becomes brittle and insoluble. This latter process leads typically to an increase of carbonaceous residue when examining such materials e.g. by non-isothermal thermogravimetry.

The changes which are invisible at the beginning occur in the artifact gradually and in final visible state there appear cracks, loss of gloss, changes of the colour, and in the case of foams the material disintegrates.

Schematically, the chemical changes in the plastics depending on the original structure of macromolecules and additives may be depicted by the Figure 2 (Grassie 1981; Matisová-Rychlá 1996).

The mode of degradation is determined by the character of the first initiating site in the polymer structure (reactions 1, 2 and 3). According to the mechanism which brings about the appearance of this initiating sites we differentiate photo degradation (photolysis), thermal degradation (thermolysis), photo oxidation or thermo oxidative degradations, which involve the assistance of oxygen, radiolytic and mechanochemical degradation, etc. Generally, plastics

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Reaction	Method / Process	No.
$PH \longrightarrow P\cdot$	w_i	1
$PH \longrightarrow$ low molar mass compounds + unsaturated polymer	unzipping	2
PH (water, H^+, HO^-) $\longrightarrow ZH$	hydrolytic degradation	3
$P\cdot \longrightarrow$ monomer$+P\cdot$	depolymerization to monomer	4
$ZH+O_2 \longrightarrow P\cdot + HO_2\cdot$ $P\cdot + O_2 \longrightarrow PO_2\cdot$	oxygen absorption	5
$PO_2\cdot +PH \longrightarrow POOH + P\cdot$	DSC, determination of POOH	6
$POOH \longrightarrow PO\cdot + \cdot OH$		7
$2\,POOH \longrightarrow PO_2\cdot +PO\cdot + H_2O$		8
$PO\cdot \longrightarrow P\cdot +$ products of lower molar mass	thermogravimetry, change of mechanical properties	9
$PO\cdot\,(\cdot OH) + PH \longrightarrow POH\,(H_2O) + P\cdot$	analysis of water, alcoholic groups	10
$P\cdot + P\cdot \longrightarrow P\text{-}P$	crosslinking	11
$P\cdot +PO_2\cdot \longrightarrow POOP$	temporary crosslinking	12
$PO_2\cdot + PO_2\cdot \longrightarrow POOP + O_2$ $\longrightarrow P{=}O^* + POH + O_2^*$	chemiluminescence	13
$PO_2\cdot + InH \longrightarrow$ non-radical products	analysis of stabilisers	14
$POOH+D \longrightarrow$ non-radical products	determination of induction time of degradation	15

Figure 2. Scheme of chemical changes occurring in plastics (P and Z denote macromolecular chains of the different length, InH is chain breaking inhibitor, D peroxide decomposer, $P\cdot$ $Z\cdot$, are polymer radicals)

may degrade under the effect of ozone, peroxides, acid and alkaline compounds, halogens or other aggressive compounds, under the effect of electric field, plasma and corona discharge, ultrasound, laser radiation, etc.

There is a particular group of degradation processes represented by polymer analogous reactions where the average molar mass remains almost unchanged initially. There occurs the splitting off of some side groups or their modification as e.g. in the case of poly(vinyl chloride) or poly(vinyl alcohol) where hydrogen chloride or water are formed by unzipping of corresponding atoms or groups from the main chain of a macromolecule and unsaturated C=C bonds remain on the polymer backbone (reaction 2).

The thermal and thermo oxidative degradation stability of a given plastic is usually determined by the rate of initiation. This can be due to the formation and appearance of C=C unsaturations, carbonyl, carboxyl, hydroxyl and hydroperoxide groups and from the formation of carbonaceous residue at higher temperatures in the case of polymers which predominantly crosslink. This can be studied e.g. from the loss of the sample mass by thermogravimetry. The most decisive and also convincing, however, are the remaining mechanical properties.

Oxygen is an important cofactor in any initiation mode in reduction of polymer stability. It is related with a fast introduction of unstable O-O bonds into the polymer structure and development of free radical mechanism according to the reactions 5-13 of the Figure 2 as it was proposed by Bolland and Gee (Bolland 1946) for auto oxidation of rubber compounds: Free radicals (P·) generated in the initiation process (reaction 1) are in the presence of oxygen converted to peroxyl radicals (PO_2·) (reaction 5) and subsequently to hydroperoxides (reaction 6), intermediate compounds which provoke chain reaction unless stabilisers (InH or D) are used to interrupt the process (reactions 14 and 15).

Thermal decomposition of dialkyl peroxides, diacyl peroxides, hydroperoxides and peracids depending on the structure of the peroxidic compound occurs in a measurable rate usually above 60ºC. Diacyl peroxides and peracids are considerably less stable than dialkyl peroxides and hydroperoxides.

Some traces of metal and metal ions may initiate the decomposition of hydroperoxides even at room temperature and contribute to the plastics degradation as well. The traces of metal ions are always present in each plastic and may affect the polymer oxidation and subsequent degradation considerably. The sequence of efficiency of metal ions depending also on the valence state and type of its ligand may be postulated as follows:

$$Cu>Mn>Fe>Cr>Co>Ni$$
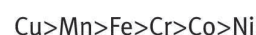
This sequence correlates well with the reactivity of these ions in Haber-Weiss cycle of hydroperoxide decomposition.

$$POOH + Me^{n+} \rightarrow PO· + Me^{(n+1)+} + ·OH$$
$$Me^{(n+1)+} + POOH \rightarrow PO_2· + Me^{n+} + H^+$$
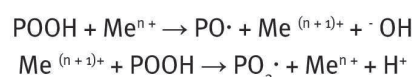
However, the mechanism for any particular ion may be more complex involving e.g. the reaction of lower oxidation state of metal ion with peroxyl radicals, etc. Ions of aluminium, titanium, zinc and vanadium usually reduce the rate of oxidative degradation.

The decompositions of hydroperoxides (reactions 7 and 8) which occur as uni or bimolecular process are the most important reactions leading to the free radical chain degradation. The bimolecular reaction takes place after some time of unimolecular initiation provided that a sufficiently high concentration of hydroperoxides accumulates. In the case of oxidation in a condensed system of a solid polymer with restricted diffusional mobility of respective segments, where hydroperoxides are spread around the initial

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A\B	C	N	O	S	Si
C	348	292	352	259	290
N	292	160	222		
O	352	222	139		369
S	259			213	
Si	290		369		

C=C 615, N=N 418, C=N 615

Figure 3. Dissociation energies of bonds A-B in kJ.mol^{-1} that may form the skeleton of the macromolecular structure in plastics

initiation site, predominating mode of initiation of free radical oxidation is bimolecular decomposition of hydroperoxides.

Reaction 9 representing β-scission of alkoxyl radicals leading to the reduction of molar mass competes with transfer of free radical centre to surrounding groups with formation of alcoholic groups (reaction 10) which subsequently loose water and C=C unsaturations appear randomly along the polymer chain.

Reactions 11-13 represent the termination of free radical sites which may have the character of crosslinking (reaction 11) and/or formation of dialkyl peroxides (reactions 12 and 13) which may act as new initiating species. The first parallel reaction in reaction 13 is typical for tertiary peroxyl radicals while the second reaction for secondary (or primary) peroxyl radicals. In the latter case, the disproportionation of peroxyl radicals takes place according to the Russel's scheme (Russel 1957) where carbonyl groups and oxygen are being formed in excited triplet and singlet states. The conversion of these excited states to the ground state occurs with lower or higher yield as a radiative process (chemiluminescence).

 At the same time, Figure 2 indicates the links of elementary reactions to the respective method of its investigation.

Heat induced degradation initiation sites proceed by the production of ions, free radicals or excited states of molecules. Their formation in the polymer depends on the average number of weak bonds in the macromolecular structure which are implemented into the polymer during its synthesis and storage. They may be related to the impurities or catalysts residues which remain in the plastic from its synthesis.

Very undesirable structural irregularities are O-O bonds that are introduced into the polymer during its storage, processing and/or during the polymerisation of monomers not sufficiently deprived from oxygen.

The average dissociation energy of bonds forming the structure of a macromolecule (Figure 3) is a primary consideration for the estimation of resulting stability of a given plastic. The fraction of bonds which reach the energy equal to dissociation energy D is determined by the Boltzman's factor

$$\exp(-D/RT)$$

where T is absolute temperature. This may be exemplified as follows: Temperature at which in one mole of C-C bonds at least one is dissociated into radicals is 486°C while in one mole of O-O bonds it is 30°C, only.
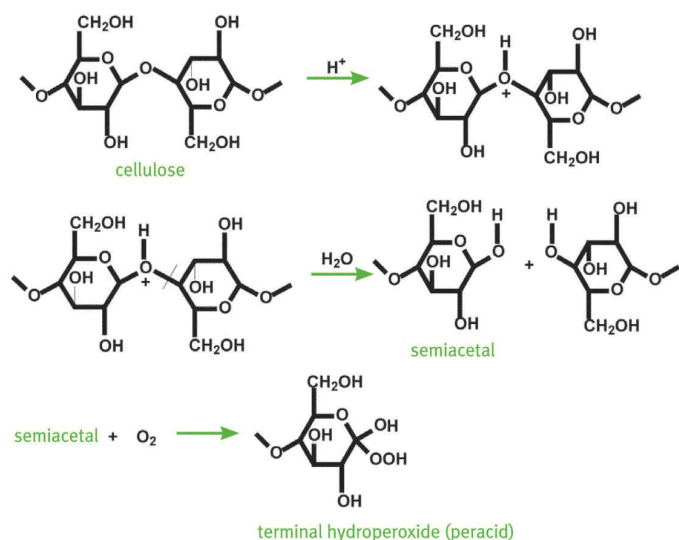
Figure 4. Acid hydrolysis of cellulose chains – example of combination of cross reaction of hydrolysis and free radical oxidation on terminal groups formed subsequently from hydrolytic attack
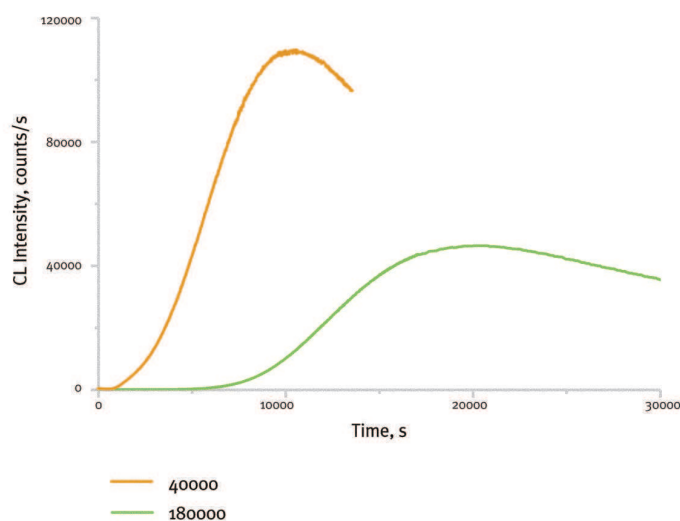

Figure 5. Chemiluminescence oxidation runs at 120°C in oxygen for polypropylene powder samples of different molar mass. The numbers associated with curves express the average molar mass in $g.mol_{-1}$

Increasing the difference in the electronegativity of the heteroatoms in the polymer main chain or in its side groups also increases the polar nature of respective polymer linkages and ionic mechanism of degradation starts to predominate. This is the case of polymers having in the structure ester, ether and acetal bonds, C-O and P-O bonds in biopolymers, Si-O bonds in polysiloxanes. Ionic degradation mechanism is less probable for amide or imide bonds, C-N and C-halogens bonds. The case of ionic degradation and subsequent hydrolysis may be seen on the case of cellulose chains where degradation starts on C-O-C groups linking the glucopyranosyl units and is initiated by hydrogen ions (Figure 4). The process of scission of oxonium ions requires the presence of water.

Oxonium ions are cleaved to terminal semiacetals which are prone to subsequent oxidation by oxygen. An easy ionic pathway of polysaccharide degradation thus opens a route for free radical oxidation of terminal groups. This is very frequent case of hydrolytic degradation mechanisms of many heterolytically degrading polymers (Rychlý and Matisová-Rychlá 2008). In the case of cellulose products it is not therefore surprising that a considerable increase of stability may be achieved by a simple deacidification process which prevents the formation of oxonium ions.

The general rule exists that the polymer with higher average molar mass appears to be more stable than that with lower molar mass. This may be ascribed to the effect of increased concentration
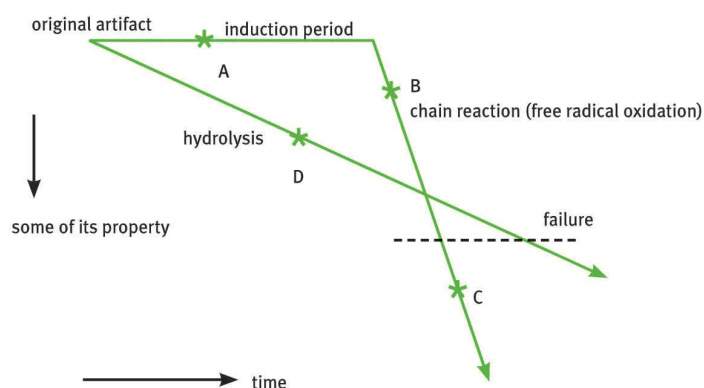
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Figure 6. Unknown points of residual stability A, B, C and D of the plastic material

of more reactive terminal groups that promote initiation of thermal oxidation (Rychlá and Rychlý 2000) (See the Figure 5).

The specificity of the assessment of degradation of plastics in museums is due to the fact that once a plastic is identified there is usually no information at which point of the degradation scheme occurs. Provided that the artifact contains plastics degrading by chain free radical mechanism (polyolefins, polyamides and polyether urethanes) it is important to know that we are somewhere around the point A of the induction period or behind the induction period (as e.g. in the point B) (Figure 6). The similar situation may occur with artefacts in which hydrolytically degrading mechanisms prevail. The best way how to find it is to test materials several times after a significant period of time of natural or accelerated degradation. The methods which have large potential to ascertain it involve non-isothermal analysis including differential scanning calorimetry (DSC), thermogravimetry and chemiluminescence. Isothermal methods at constant temperature are advantageous for stabilised polymers with a tendency to degrade by chain free radical mechanism via hydroperoxides where an induction period under certain conditions is a clear indication of the remaining material stability. The above methods differ in the sensitivity to trace some change due to the degradation. Of them chemiluminescence (Ashby 1961; Barker 1965; Malíková *et al.* 2010; Rychlá and Rychlý 2000; Rychlý and Matisová-Rychlá 2008; Schard 1964; Wendlandt 1984) takes evidently the sensitivity number 1, then thermogravimetry and DSC follow.

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