Degradation study on polymeric materials used for design manufactures

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Anno Accademico 2012-2013
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In the present work of thesis a study on the degradation of five different polymers, Polyvinylchloride, Acrylonitrile butadiene styrene, Polypropylene, High-density Polyethylene and Linear low-density Polyethylene is presented, examining in depth the degradation mechanism and consequences of UV light exposure. It was chosen to simulate solar light degradation in order to acquire information that could be used for the investigation of real cases. In particular during this work, the conservation conditions and mechanism of degradation of two 1960’s design desk lamp were studied.

Specimens of the previously listed polymers were subjected to an accelerated aging process using an Arc Xenon lamp, and degradation was monitored at several time intervals until a maximum of 700 hours, in the case of PVC, or, for the remaining plastics, 1000 hours of aging.

All the specimens were analysed with traditional methods of characterization, such as FTIR spectroscopy, Microscope observation, Colorimetric analysis and SEM analysis. Furthermore an innovative method of analysis, the scratch test, was used to support the characterization. With this kind of test, variations in the mechanical properties of the most superficial layers, as a consequence of degradation, can be detected, such as changes in hardness, ductility or brittleness. This technique is of great interest because it is micro-invasive and provide information that it is not possible to obtain with the other more traditional techniques.

Comparison between the results of characterization analyses at different aging time are shown for each polymer and discussed in terms of their degradation development.

The analyses carried out on the two case studies were aimed at defining their constituent polymers and conservation conditions. Moreover an analysis of samples taken at increasing depth from the surface was performed in different areas of the lamps, allowing to draw consideration about the degree of degradation for each significant area of the lamps.

In the final part of this research work, some preliminary tests were performed on the most aged specimens with the purpose of defining new conservation treatments for design manufactures collected in museum. In particular some additives were tested with the scope of reducing the surface yellowing, one of the more evident consequences of photo oxidation.
ABSTRACT

Nel presente lavoro di tesi viene presentato uno studio sul degrado di cinque differenti polimeri, Polivinilcloruro, Acrilonitrile butadiene stirene, Polietilene ad alta densità e Polietilene lineare a bassa densità, esaminando in particolare il meccanismo e le conseguenze dell’esposizione alla luce UV. È stato scelto di simulare il degrado dovuto alla luce solare al fine di acquisire informazioni utili allo studio di casi reali. In particolare, durante questo lavoro sono state studiate le condizioni di conservazione e il meccanismo di degrado di due lampade di design degli anni ‘60.

Campioni dei polimeri elencati precedentemente sono stati sottoposti a un processo di invecchiamento accelerato utilizzando una lampada allo Xeno, e il degrado è stato monitorato a diversi intervalli di tempo fino a un massimo di 700 ore, nel caso del PVC, e di 1000 ore per le plastiche rimanenti. Tutti i campioni sono stati analizzati con i metodi di caratterizzazione tradizionali, quali la spettroscopia FTIR, l’osservazione al microscopio, l’analisi colorimetrica e l’analisi SEM. Inoltre, un metodo investigativo innovativo, lo scratch test, è stato usato per rafforzare la caratterizzazione. Con questo tipo di test posso essere identificate variazioni nelle proprietà meccaniche dello strato più superficiale dovute al degrado, come cambiamenti relativi alla durezza, alla duttilità o alla fragilità. Essendo micro-invasiva questa risulta essere una tecnica molto interessante e fornisce informazioni che, con tecniche tradizionali, sarebbero difficili da ottenere. Per ogni polimero, vengono mostrati confronti tra i risultati delle analisi di caratterizzazione per diversi tempi di invecchiamento e discussi in termini di sviluppo del degrado.

Le analisi svolte sui casi studio sono state volte a definire i polimeri costituenti e le condizioni di conservazione. Inoltre, lo studio di campioni prelevati sia superficialmente che in profondità in varie zone delle due lampade hanno permesso di trarre considerazioni circa lo sviluppo del degrado per ciascuna area significativa delle due lampade.

Nella parte finale di questo lavoro di ricerca, sono stati svolti test preliminari sui campioni più degradati con lo scopo di definire nuovi trattamenti di conservazione per manufatti di design presenti nei musei. In particolare sono stati testati alcuni additivi al fine di ridurre l’ingiallimento superficiale, una delle conseguenze più evidenti della foto ossidazione.
1. Introduction

Since their introduction, at the end of the 19th century, synthetic plastics had a significant influence on a wide range of aspects of everyday life, from industrial to domestic and cultural, becoming therefore an important element of our cultural heritage. The first semi-synthetic plastics (e.g. cellulose nitrate) were designed to imitate luxury materials, such as tortoiseshell and ivory. After world war II, as a reaction to the restrictions on imported natural materials (e.g. wool and silk), many new polymers were introduced including polyethylene, polyamides, Poly(methyl methacrylate), Polyurethanes, Polyvinylchloride, Polytetrafluoroethylene and Polystyrene.

During the 1950’s a number of new thermoplastics, characterized by valuable and useful properties, became available, such as High-density polyethylene or Polypropylene that soon became a largely widespread thermoplastic. Afterwards, more specialised materials were developed, as polycarbonates or ABS polymers, that resulted from studies on the high-impact resistance of polystyrenes.

In 1960s plastic industries around the world and production reached levels of order of magnitude higher than 20 years before.[1]

1.1 Plastics diffusion

The undeniable ease of diffusion for plastics, since the 20th century, can be justified by their particular chemical, physical and mechanical properties, the wide range of methods for manufacturing, the typical lightness and the low cost.

For example, plastics have been widely accepted as packaging materials. Plastic bottles have been particularly appreciated for their lightness and have been favoured to the glass, whose fragility had frequently led to damaging consequences. The ability of many polymeric materials to withstand some very corrosive chemicals has been of benefit to the chemical and related industries. Plastic items are also widely used in the medicine field taking advantage from their chemical stability and, in some cases, biocompatibility.

Nowadays the automotive industry is one of the major users of plastics, whether for car electrical equipment such as batteries, plugs, or for interior body trim and, recently, also for drain plugs or petrol tubing. Plastics also find increasing use in vehicles for both water and air transport.

Domestic and commercial furniture form another important and extended market. Its diffusion include stacking chairs, armchair body shells, foam upholstery, desks, kitchen equipments, lamps and other home furnishing.

As plastics diffusion increased, also the number of artists and designer that choose plastic materials for their artistic works increased. The explanation can be found in the appreciable properties reported before, as well as the ease in moulding, and colouring with pigments and dyes.
Plastics are becoming more and more a significant part of collections of many artistic and scientific museums. Of great interest are both artistic plastic objects and items of historical and cultural interest realized in plastics. The latter include all that plastic manufactures that testify the evolution of science and technology, an innovative industrial design or the production of new advanced materials.

As an example can be considered the process of substitution of ivory with celluloid for hair combs or with ABS for piano keys, as well as plastic jewels, vinyl records or household items. A clear and obvious consequence of what just stated, is that a good conservation of plastic artefacts present in museum is indispensable.

### 1.2 Conservation of plastics

Once plastics reach collectors and museums, they often become a complex problem for conservators; this is because plastics deteriorate faster than many other materials in museum collections and have a useful lifetime that typically ranges between 5 and 25 years [2].

#### 1.2.1 Most frequently collected plastics

Polymers that can mainly be found in museum collections according to Shashoua [2], are listed in the following scheme (Tab 1.1).

<table>
<thead>
<tr>
<th>PLASTIC</th>
<th>POSSIBLE APPLICATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetate (CA)</td>
<td>photographic film, packaging films, hair combs</td>
</tr>
<tr>
<td>Cellulose nitrate (CN)</td>
<td>photographic film, bicycle parts, puppets and dolls</td>
</tr>
<tr>
<td>Epoxy</td>
<td>adhesives, surface coatings, vehicle and aircraft parts</td>
</tr>
<tr>
<td>Phenol-formaldehyde (Bakelite)</td>
<td>electrical insulation, radio and television housings, telephones</td>
</tr>
<tr>
<td>Polymides (PA) Nylon</td>
<td>woven textile, fishing line, electrical housings, reinforcing material</td>
</tr>
<tr>
<td>Polycarbonate (PC)</td>
<td>CDs, DVD, flat roofs, motorcycle helmets</td>
</tr>
<tr>
<td>PET</td>
<td>fizzy drink bottles, audio and video film, credit cards, clothing</td>
</tr>
<tr>
<td>Polyethylene (PE)</td>
<td>containers, food packaging films, carrier bags</td>
</tr>
<tr>
<td>PMMA</td>
<td>optical equipment, contact lenses, aircraft windows</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>food containers, pipes, cable insulation, furniture shells</td>
</tr>
<tr>
<td>Acrylonitrile-butadiene-styrene (ABS)</td>
<td>computer cases, telephones, casing for domestic electrical equipment</td>
</tr>
<tr>
<td>PTFE</td>
<td>non-stick cookware, water repellant textiles, wire covers</td>
</tr>
<tr>
<td>Polyurethane (PUR)</td>
<td>fibres, rubbers, rigid and flexible foams</td>
</tr>
<tr>
<td>Poly (vinyl chloride)</td>
<td>rigid PVC (window frames) plasticized PVC (flexible tubing)</td>
</tr>
</tbody>
</table>

Tab 1.1 Frequent museum collection plastics

There are typical signs of degradation, characteristic of all plastics that indicate the need of conservation and restoration approaches.
Among these, as an example, the following can be cited: abrasions, breaks, cracks or the presence of chips as consequences of physical damage due to use; chalking, due to separation of pigment or fillers from the polymer, discolouration and yellowing, due to the formation of cromophores (further explanations will be found in chapter 2).

1.2.2 Identification of Plastics

The preservation of plastic artifacts, therefore, depends on a fairly accurate identification of the polymer of which it is made. This is not a simple task; in fact it’s hard to identify the type of modern plastic only by appearance and feel, especially where dyes, pigments, stabilizers, plasticizers or other additives have been added to the base polymer, which can modify or mask its general properties.[3]

Most plastics can be identified via simple destructive tests such as studies on the behaviour of polymers on impact, in liquids or in a flame. As an example, the position of a plastic sample in a beaker of a test liquid with known density at a particular temperature is related to the density of the plastic, which is dependent on the weight of molecules and the way they pack. So, if the chosen liquid is water (density 1 g/cm), it can be observed that Polyethylene, Polypropylene and polystyrene float, while other plastics sink [2]. Another interesting method of inspection concern the plastics’ hardness; those that can be marked with a fingernail include polyethylene, polypropylene, plasticized PVC and polyurethane while other types are not affected. Even tapping on the plastic surface some information can be deduced, indeed, if the sound is metallic, the plastic is likely to contain polystyrene [2].

Obviously, simple destructive tests are not an option for objects of cultural heritage. To solve this problem many scientific methods for identifying plastics more reliably have been detected. The most useful are those that reveal the chemical composition of a material from microscopic sample sizes, or even via non-invasive, in-situ techniques.

Spectroscopic and chromatographic techniques such as Fourier transform infrared spectroscopy (FTIR) and pyrolysis-gas chromatography-mass spectrometry (Py-GCMS) are extremely useful for the identification of plastics. Since the 1990’s spectroscopic techniques have improved significantly in terms of the size of sample required, the speed of analysis, the user interface, and portable /mobile instrumentation. The use of these spectroscopic methods has become widespread in conservation and it is likely to increase further with the recent development of handheld instruments for rapid, non-invasive, in-situ analysis. [3]

1.3 Aim of this work

The aim of this work is to study degradation phenomena and mechanism of some classes of polymers in a specified environment in order to better understand and identify the degradation state of plastic objects which, feasibly, were subjected to similar conditions. For this purpose analyses on well-known specimens is demanded.

Plastic specimens of Polyvinylchloride, ABS, Polypropylene, High-density Polyethylene and Linear low-density Polyethylene, were chosen for these studies. These specimens, of known
chemical composition, were submitted to accelerate aging using a Xenon lamp and tested with destructive and non-destructive tests. Specimens were investigated before accelerated aging and at different grades of degradation, in particular, a fixed number of specimens have been taken off the solar box after 100, 250, 500 and 700h, for PVC, or 1000h for the remaining plastics.

Characterisation studies include spectroscopic (FTIR) and microscopic (portable and stereo microscope, SEM) and also mechanical analyses (micro scratch tests)

The results obtained from the analyses carried out on these plastics, were combined with investigations on real case studies’ condition; two 1960’s design desk lamps made of ABS and Polypropylene.

Moreover, innovative tests have been started on the aged specimens, concerning the absorption of few additives on their surfaces. It is known to all the importance, and also the ease, of using additives in the polymers blend, giving to the polymer better mechanical, physical, chemical and also aesthetical properties. Rarely, however, they are used on already existing plastic manufactures due to their difficult absorption, in fact it definitely constitute an innovative topic of study

In the field of plastic’s object restoration and conservation it could be relevant the recovery of mechanical properties as toughness but also aesthetical ones like, for example, the whitening of surfaces yellowed by photo oxidation.

These investigations certainly constitute the topic of future developments.

1.4 Case studies

As real degraded plastic objects two lamps designed in the ‘60 were considered. The first one is a red “Telegono” desk lamp, designed in 1968 by Vico Magistretti for Artemide; made by ABS for the structure and the compartments, and PP for the light globe. The other desk lamp is the white “KD 4335” designed by Giò Colombo for Kartell and made using ABS.
1.5 Standard plastics and their diffusion

The polymers chosen as standard samples are Poly (vinyl chloride), ABS (acrylonitrile butadiene styrene), Low-density Polyethylene, High-density Polyethylene and Polypropylene. These types of polymers were chosen as significant and representative for their huge diffusion and usage by industries and artists, and also for their chemical and physical properties.

1.5.1 Polyvinylchloride (PVC)

Poly(vinyl chloride) (PVC) has the advantage of low cost, long-term stability and flame resistance among other plastic products, moreover the mechanical properties of PVC can be controlled from soft material to hard material by varying the amount of plasticizer in the blend. In museum collection it can be found in clothes and footwear, furniture, electrical insulation, in housewares and toys; consequences of degradation can be seen in 5-10 years only. PVC is usually modified with plasticizers, semi-volatile solvent materials that if incorporated in the polymer can increase its workability, flexibility and elongation.
Plasticizers are weakly bonded to the polymer chain, this is why they can easily migrate during degradation.

1.5.2 Acrylonitrile butadiene styrene (ABS)

ABS is an economical general purpose polymer used in a wide variety of applications. It is a copolymer of styrene and acrylonitrile modified with butadiene rubber which acts as a filler. The first ABS resins were produced in the fifties. Their properties are tenacity, crash resistance and a hard surface, this is why they are mainly used for furniture, toys, car parts, television sets and radios.

1.5.3 Polyethylene (PE)

It is one of the most diffuse and well-known plastics. It is usually found in three degrees of density: low, medium or high; recently linear low density polyethylene has been developed which has better characteristics with respect to the traditional low density product. For example it has higher tensile strength and higher impact resistance than LDPE as well as better environmental stress cracking resistance. Polyethylene’s advantages can be found in its low cost, easy manufacture, tenacity and flexibility at low temperatures, moreover it is a good insulator, odourless, untotoxic and transparent. It is frequently used in household goods, toys, cable, bottles, protective film, and tubing.
1.5.4 Polypropylene (PP)

It is one of the more recent plastics, syntetized by G. Natta and K. Ziegler in 1954. They found out that, varying the form of the catalyst, different types of polypropylene could be produced, discovering that isotactic polypropylene exhibited particularly useful properties. Natta and Ziegler both won the Nobel Prize for Chemistry for the development of what are now known as Ziegler-Natta catalysts. Polypropylene has low density and low strength but poor impact resistance. It is characterized by high melting temperature (around 170°C) and maintains its rigidity up to 100°C; it is very resistant to abrasion and heat, has excellent dielectric and insulating properties, and fatigue resistance. There are several types of propylene on the market. It is used in many applications as sanitary articles, electrical appliances, toys, cars, sports, food containers, furniture and components for the chemical industry.
2. Aging of plastic materials

Polymers can lose their features as a result of several types of degradation, some more harmful than others. The probability of degradation is reduced if a museum environment is considered, but a lot of possible damaging situations still remain. In the following section a brief illustration of more frequent degradation mechanism is described, with particular attention to the consequences of an extended period of light exposure, since this is the type of degradation chosen for the artificial weathering of the samples.

2.1 Plastic degradation

The degradation of plastics consists of any change which has adverse effects on its properties or function. In general plastics, after manufacture, have an induction period that is followed by a period during which irreversible damage can be observed and measured. This period continues until the end of the useful lifetime for the object is reached. Usually the shift from induction to degradation period is brief so plastics can change from a good condition state to a degraded one in only 6 months. [2]

We can identify two phases in the life cycle of plastic where degradation can occur easily: the higher probability of degradation is achieved during the manufacture phase and during plastic utilization; in fact when the material is molded or extruded it is subjected to high temperature which can help thermal and oxidative degradation. In the same way, during use plastic is exposed continually to air, moisture, light and heat which lead to chemical changes in the polymer.

As can be deduced, the causes of degradation for plastic objects are multiple; a list of the most frequent situations can be compiled.

2.1.1 Degradation due to mechanical factors

This type of damage mostly results from the object usage prior to collection, for example it may have been bended or distorted several times, or it may have been accidentally scratched. Two are the main consequences: an embrittlement of the object and, where microcracks are present, an increase in the absorption of moisture, pollutants or other chemical with which the object get in contact leading to a possible local chemical degradation.

2.1.2 Degradation due to thermal factors

In general an increase in the rate of degradation with an increase in temperature can be observed. This phenomenon is explained by the Arrhenius equation, which states that the rate of a chemical reaction (degradation) will double with each 10°C. In fact, some polymers have been observed to double their rate of oxidation with a temperature increase as small
as 8°C [4]. Heating plastics provides sufficient energy to break bonds in the backbones or side chains of polymers in the same way of light; this depolymerization result in a measurable loss in mechanical properties.

A more direct and visible consequence of heating some plastics above the glass transition temperature is that they become more flexible and can flow and distort on handling. These consequences are known as thermal decomposition of the plastic, no chemical reactions are involved. Physical degradation can be seen also cooling plastics and result in the object tendency to contract, shrink and become stiffer and brittle. Worst consequences are observable on composite materials, made from two or more constituent materials with significantly different physical or chemical properties, that when combined, produce a material with characteristics different from the individual components. When submitted to critical high or low temperature each constituent material try to shrink or expand freely due to its particular thermal expansion coefficient, but is restrained by the material with which is in contact. Differential shrinkage may cause failure of one material unless the stress introduced by the temperature change is absorbed by elastic or inelastic deformation.

2.1.3 Degradation due to chemical factors

Reaction of plastic with chemical agents as oxygen, ozone, water, metals, organic solvents and light radiation provide sufficient energy and appropriate environment to break selected chemical bonds present in the polymer and additives. Polymers can be subjected to oxidation, for example, during manufacture as well as during storage and use; it can take place under room temperature but it is accelerated if the environment provides also heat and light. The degradation caused by chemical agents result in structural changes such as chain scission, crosslinking, development of cromophores and polar groups.

2.1.4 UV degradation

Light, especially high-energy ultraviolet radiation, is one of the main factors that can initiate or accelerate degradation of all plastics. UV energy absorbed by plastics can excite photons, which then create free radicals that means a break in the carbon-carbon, carbon-oxygen or carbon-chlorine bonds in the polymer chain via mechanisms known as Norrish Type I or II. This can happen because UV light with wavelength lower than 400 nm correspond to an energy amount higher than 300 kJ, that is the same order of magnitude of most polymer bonds.
The degradation after UV exposure is due to combined effects of photolysis and oxidative reaction. In an inert atmosphere this kind of degradation would be slow, what is more important is the fact that, in real conditions, air is always present and lead to a photo oxidative reaction, which is very harmful. Photo-oxidation can only occur when chromophores are present in the polymer; those chemical groups can absorb wavelength higher than 290 nm which are able to cause a dissociative process resulting in degradation. Chromophores can be aromatic groups present in the polymer backbone, impurities from manufacture, defects and weak bonds (C=C and C=O for example are those most susceptible to photodegradation). According to the Lambert-Beer law, the amount of absorbed light depends on the extinction coefficient of the chromophores, their concentration and the thickness of the sample. As a consequence of its absorption, light introduces chemical changes but also causes dyes and colorants to fade. The chemical mechanism is a radical-based autooxidative process. In the initiation step, due to the absorption of photons, free radicals are generated and, since air is present in the atmosphere, they react with oxygen giving peroxy radicals that, with other polymeric molecules gives hydroperoxides and other alkyl radicals. The rate of reaction of oxygen with alkyl radicals is very high and is largely determined by the ease of hydrogen abstraction. For PE the secondary hydrogens are the most labile, for PP the tertiary ones[10]. During a step called chain branching the hydroperoxides can decompose into alkoxy and hydroxyl radicals which can initiate another propagation cycle; some hydroperoxide decomposition mechanisms can even lead to radicals and chain scission. The termination step usually occur through the reaction of two peroxy radicals; for PP the termination reaction for tertiary peroxy radicals lead to the formation of dialkylperoxides, while for PE the secondary peroxy radicals result in an alcohol and ketone[10/11]. Oxidation products are always developed during photooxidation mechanism, in fig 2.2 some of the PE’s oxidation products are shown [9].
These chemical reactions, moreover, usually lead to variations in mechanical properties. For example, considering PP, one of the consequence of its degradation is chain scission and thus loss of molecular weight. According to Schoenberg [19], for most polymers at low molecular weight correspond high embrittlement; in a certain Mn (average molecular weight) range, fracture toughness decreases linearly with $1/Mn$.

Further consideration must be done considering the case of ABS and PVC photo-oxidation. The pathway by which degradation of PVC takes place includes, in addition to chain scission and crosslinking, an important reaction that is the evolution of hydrogen chloride (dehydrochlorination).

Dehydrochlorination occurs at imperfections and starts with the breaking of a C-Cl bond, followed by abstraction of a hydrogen atom and a shift of electrons in the polymer to form a double bond. The next chlorine becomes highly reactive and so it is removed, this happens along the whole chain in an “unzipping” process: the result is the formation of a conjugated polyene system accompanied by the formation of hydrogen chloride (fig 2.3). As the conjugated structure develops, the polymer begins to absorb radiation in the ultraviolet. Dehydrochlorination is an autocatalytic reaction, so the degradation rate is accelerated until hydrogen chloride is removed.
The growing of degradation is observable even without analyses, just looking at the color of the sample surface: it changes from white to yellow to brown and, ultimately, black. The degradation's result depends both on the polymer itself and the plasticizer, and are strictly correlated to each other. Besides PVC, ABS is one of the plastics that is mostly subjected to photo oxidative degradation which occurs both in the polybutadiene (PB) and in the styrene acrylonitrile (SAN) phase.

Upon exposure to UV radiation, photolysis of the methylene bond in the trans-1,4-polybutadiene structure occurs, producing an allylic radical polymer chain. This radical may undergo several reaction paths to yield further radicals, together with oxygenated species such as hydroperoxides, ketones and esters.[6] The thermal and photochemical homolysis of α,β-unsaturated hydroperoxides has been shown to occur according to the two following mechanisms [8]:

![Fig 2.4 Homolysis of α,β-unsaturated hydroperoxides](image)

Photo-oxidation of the PB phase is thought to be the major cause of mechanical property deterioration in ABS indeed, while the Styrene component influences the stiffness and processability, AN influences the rigidity, toughness, and improves the dynamic load-bearing and impact strength while the PB component imparts impact resistance to the brittle thermoplastic matrix. [16]

Salari et al. [17] studied the effect of weathering on the flow, microstructure and physical mechanical properties of ABS, and the results showed a significant decrease of impact strength and elongation at break in the first stages of UV exposure.

During degradation cross-linking occurs in the rubber phase as principal effect of irradiation reducing the difference with the modulus of the SAN based matrix. Since the two phases has different physical characteristics, the result is a different fracture behavior. The irradiated side became more brittle and the modulus increase in a behaviour form known as “ductile to brittle transition” [17]

The loss in elastomeric properties of ABS has been explained in terms of scission reactions of the graft of PB with the rest of the polymeric matrix [18].

Furthermore, UV exposure of ABS leads to its discolouration: both the SAN phase and the PB phase can form cromophores upon oxidation which absorb energy in the UV visible spectrum and cause discoloration, an initial color fading after UV exposure is due to oxidation in the SAN phase, subsequent yellowing is due to the PB phase [13].
2.1.5 Other degradation’s causes

Those polymers that are synthesized by condensation process can undergo to the reverse reaction, in the presence of water molecule that lead to bonds break (hydrolysis). Hydrolysis is usually initiated by acidic or alkaline, the most vulnerable polymers are cellulose nitrate and acetate, polyesters and polyester-based polyurethanes while polyethylene and polypropylene are highly hydrophobic. Furthermore, polymers tend to become more polar when oxidized, so their sensitivity to water increase with aging. The consequences of this degradation mechanism is chain scission at numerous sites, leading to a reduction in molecular weight and loss of mechanical properties.

Also biological factors can affect polymers degradation even if it’s not so frequent; polymers, indeed, are not themselves prone to biological degradation but it can, however, take place when microbial enzymes chemically break down large molecules into smaller fragments which are water-soluble.

Another source of degradation can be found in traces of metals which can come in contact with polymers during processing, transporting or shaping, because, in fact, many metal ions catalyze oxidation by accelerating decomposition of hydroperoxides at room temperature. For example copper is a highly effective catalyst for semi-synthetic materials, in general their effectiveness as catalysts depend on their oxidation states.

2.2 Accelerated ageing

During accelerated aging the processes of deterioration are speeded up in the laboratory in order to elucidate the mechanism of degradation, that is the chemical reactions involved and, therefore, the physical consequences. It is an important technique for discovering if the degradation process accelerate in time, if there is an induction period, and what happen during the different stages.

The accelerated aging is an essential part of the degradation studies, it permits the monitoring of all the features changing during the test, above all the chemical changes that are ultimately responsible for the physical variations of materials. Moreover it is useful to predict the lifetime of specific materials in a particular condition and to determine their useful life span.

In the conservation field, accelerated aging can be used to determine if a particular conservation treatment can last in time and its long time effects. The accelerated aging can be achieved in several ways according to the conditions that are to be established, for example materials can be tested with particular levels of stress, changes in temperature, humidity, pressure. In this work the aim was to recreate the conditions that could be found in a museum setting and therefore the exposure to UV light through an arc xenon lamp has been chosen. The xenon lamp, indeed, is usually used to simulate sunlight and it’s usually employed in solar cell testing and solar simulation for age testing of materials.
3. Materials and methods

3.1 Case studies

Samples were taken from the two design objects choosing the more significant areas of the items both intact areas, in order to identifying constituent polymers, and degraded ones. Sampling was performed by using a lancet; the samples were kept separated in weighing papers and hence stored in PE cases.

Micro samples of “Telegono” lamp were obtained from the external structure taking advantage from a pre existing crack, from the compartments, and from the light globe. For each of these areas samples were taken both from the more external surface and from a deeper one in order to have representative samples of the more degraded and original material.

Micro samples of “KD 4335” were taken from four different areas.

“A” and “B” areas are representative for the degraded and natural plastic, depending on the depth of the sample taken. They belong to the external surface of the lamp.
“D” and “C” areas belong to the internal surface of the lamp and so were in contact only with the hypothetical light globe.

Fig 3.3"KD 4335” samples

3.2 Reference materials’ samples
The reference materials used in this work are:

- Poly vinyl chloride (PVC)
- Acrylonitrile butadiene styrene (ABS)
- Polypropylene (PP)
- High density polyethylene (HDPE)
- Linear low density polyethylene (LLDPE)

All the specimens were provided by POLIPLAST srl, a except for LLDPE provided by Versalis S.p.A.

PP, LLDPE and HHDPE samples have been cut from a larger plate in pieces of two different dimension: 14 samples measures 3x2,5 cm while 8 samples 2,5x1,5.

18 ABS samples have been obtained from specimens for mechanical tests and each piece is 2x3 cm

The PVC samples have dimensions equal to the other plastics but a greater number of pieces have been obtained (77), this is because one set of aging is focused only on PVC since HCl, dangerous for its interaction with the surrounding area, is developed during accelerated ageing.

The whole samples have a thickness of 4 mm.

Each sample was cleaned with ethanol and dried in a stove set at 40°C
3.3 **Ageing**

3.3.1 **Accelerated Ageing**

Accelerated ageing has been carried out using a Suntest CPS+ apparatus equipped with a Xenon arc lamp source and a cut off filter for wavelengths below 290 nm, irradiation was kept constant at 765 W/m², at a distance of 20 cm and temperature was maintained at 35°C. Two aging sections have been conducted, in the first one only PVC samples have been aged while in the second the remaining plastics have been tested.

**First set:**
77 PVC samples have been located in the chamber in order to occupy the whole available area. After 100 hours of exposition, three specimens have been taken off the chamber; equal procedure has been followed after 250 and 500 hours. The remained samples have been aged for 750 hours. In this section only PVC samples were used because during the aging process a chemical reaction called dehydrochlorination take place, this means that hydrochloric acid is produced which can affect the other plastics.

**Second set:**
22 samples of PP, 22 HDPE, 22 LLDPE and 18 ABS samples have been positioned in the chamber. After 100, 250 and 500 hours, two ABS and three samples of the other plastics have been removed while the remaining samples remained in the chamber up to 1000 hours of aging.

3.3.2 **Natural Ageing**

A section of natural weathering was just started and it is planned to last for a year. PVC and ABS specimens were chosen for this test, as the more susceptible to degradation among the polymers studied in this work. Six specimens for each polymer were positioned on the roof of Chemistry, Material and Chemical Engineering Department branch “Mancinelli” (Polytechnic University of Milan), located at Latitude 45°29.4’ and Longitude 9°13.6’. The specimens are south oriented and inclined with an angle between 30° and 45°. The average, for each month, of the global solar radiation per day on a 30° inclined surface, in MJ/m² is shown in the following picture (fig 5.21). [22]
3.4 Characterization

Each sample has been characterized in the same way through microscopic observation, spectroscopic techniques, mechanical and colorimetric tests.

3.4.1 Fourier Transformed Infrared Spectroscopy (FTIR)

When infrared light (4000-200 wavelengths per cm) is passed through a sample of an organic compound, some of the frequencies are absorbed while other are transmitted through the sample. During the radiation exposure, at specific frequencies that correspond to particular energies, chemical bonds can vibrate. This vibration or rotation between atoms results in a net change in the dipole moment; when the charge distribution of the two atoms is different, the fluctuations in dipole moment produce an electric field that can interact with the electric field of the IR radiation, resulting in its absorption. Plotting absorbance (or transmittance) against frequency or wave number we obtain an infrared spectrum. At stronger bond between vibrating atoms correspond a higher value of wavenumber.

The Fourier transform is a mathematical operation used in the data processing, this is why the method is denominated Fourier transformed infrared spectroscopy.

A large polymer molecule has a multitude of localized dipole moments and therefore produces a rich IR spectrum, each functional group is responsible for absorption at a specific frequency.

This kind of spectrum can be used to compare the examined polymer with a database of known spectra so that it could be identified or, if the polymer is known, it is easy to find out the variations depending, for example, on the aging of the plastic.
Two different methods are equally useful depending on the sample: in transmission method the beam passes through the sample, while in reflection methods the changes in the IR beam as it is reflected by the sample is measured. Contemporary FTIR analyses couples a microscope to the spectrometer for the analysis of minute sample, this is very useful in the analysis of art objects where the samples should be as small as possible.

The traditional preparation technique is the one in which sample is finely ground into potassium bromide powder before pressing into a tablet one centimeter in diameter or a smaller micropellet but it is rarely effective for plastics.

The IR spectra for liquid components were achieved depositing the liquid slowly, using a pipette, on the surface of a KBr window and subsequently analyzed with FTIR technique.

The introduction of the diamond cell allowed solid samples to be analyzed via transmission methods. A minute portion of the solid is clamped between two diamond surfaces under pressure so that a very thin film is produced. At this point the two surfaces are separated and the one on which the film portion is bigger is examined.

It is possible to analyze directly the solid plastics without any sampling using reflectance techniques such as the attenuated total reflectance (ATR). If the object is small enough then the ATR accessory (a diamond or Ge crystal) is put in contact with the surface of the object and the pressure increased until an acceptable spectrum is obtained. Germanium has a higher refractive index than most plastics so when the beams come in contact with the sample it penetrates only 2 μm into the material before being totally internally reflected by it; the resulting beam is then directed into the detector. The detector examines the frequencies absorbed compared with those present in the incident radiation and produces a spectrum.

Spectra of polymers obtained using ATR accessory and those from a KBr tablet or Diamond cells look similar and can be compared directly; however the position of wavelengths may be shifted by 5 cm\textsuperscript{-1} moving from an ATR spectrum to a KBr one.

For the analyses of all the plastic samples listed before, an ATR method has been followed; the FTIR analysis was carried out using a Nicolet 6700 spectrophotometer coupled with a Nicolet Continuum FTIR microscope equipped with an HgCdTe detector cooled with liquid nitrogen.

The obtained spectra have been analyzed and corrected using the Omnic software and, in order to have a better comparison between spectra of the same material at different aging time, they have been normalized setting the absorbance of a specific peak to desired value. PVC spectra have been normalized on the CH twist vibration at 1330 cm\textsuperscript{-1}, ABS spectra on the CN stretching vibration at 2237 cm\textsuperscript{-1}, PP spectra on the methylene group at 1456 cm\textsuperscript{-1}. The chosen peaks have been assumed not to change during ageing.
3.4.2 Microscope analyses

An initial investigation on the surface variations between specimens has been done using a digital microscope, Dino-Lite supported by a Dino Capture 2.0 software, at two order of magnifications.

The surface of specimens has been then observed with a Leica M205C stereomicroscope equipped with a Leica DFC 290 video camera. Studies on the surface morphology and comparison between different aging time have been carried out at different magnifications.

A further analysis has been made using a Scanning Electron Microscope (SEM), that is a type of electron microscope that gives the image of a sample by scanning it with a focused beam of electrons.

The sample surfaces were analysed using a ZEISS EVO 50 EP instrument. Photomicrographs were taken at different magnifications using a Variable Pressure Secondary electron (VPSE) and a backscattered electron detector (QBSD).

3.4.3 Mechanical test – scratch test

The mechanical test chosen is the scratch test, that consists in making a scratch on the polymer surface by moving a hard instrument (scratch tip) of specified geometry under specified conditions of load and speed and then assessing the result.

The scratch performance of polymers has caught significant attention in the past few years because of their greatly expanded usage in the electronic, optical, household, and automotive applications, where long term esthetics is important. Unlike ceramics and metals, polymers are particularly susceptible to visible surface deformation and damage, even under low contact loads. Various scratch induced damage features, such as mars, fish-scales, parabolic cracks, and material removals have been observed from a wide variety of polymeric materials. [12]

A micro scratch tester (CSM instruments) was used and two different sets of parameters were chosen, as specified in the following tables. Particular attention was given to the scratch tip choice; indeed, for the first set of tests a Rockwell conical tip with 120° apex angle and 200 μm spherical tip was used in order to investigate variations in mechanical properties. In the second set a spheroid conical diamond tip with a 90° apex angle and 20 μm radius in order to achieve the highest damage condition on the specimen.

With a scratch test several data can be obtained, the penetration depth (Pd), the residual depth (Rd), the tangential force (Ft) and the acoustic emission. Moreover a friction coefficient (μ) was calculated as the ratio between the tangential and normal force.
The first type was applied on PVC only (unaged, and after 500 and 700 hours of aging), while the second on the whole range of plastics (unaged and after 1000 hours of aging).
All the specimens were cleaned with alcohol and dried before each test.

1st set:
Linear Scratch

<table>
<thead>
<tr>
<th>Type</th>
<th>Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (N)</td>
<td>2.5, 10, 25</td>
</tr>
<tr>
<td>Scanning load (N)</td>
<td>0.03</td>
</tr>
<tr>
<td>Speed (mm/min)</td>
<td>60</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>3</td>
</tr>
<tr>
<td>AESensitivity</td>
<td>9</td>
</tr>
<tr>
<td>Acquisition Rate</td>
<td>50.0 [Hz]</td>
</tr>
<tr>
<td>Type of indenter</td>
<td>Rockwell</td>
</tr>
<tr>
<td>Serial number</td>
<td>E-025</td>
</tr>
<tr>
<td>Material</td>
<td>Diamond</td>
</tr>
<tr>
<td>Radius (µm)</td>
<td>20</td>
</tr>
</tbody>
</table>

Tab 3.1 1st set scratch test parameters

2nd set:
Linear scratch

<table>
<thead>
<tr>
<th>Type</th>
<th>Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (N)</td>
<td>25, 10</td>
</tr>
<tr>
<td>Scanning load (N)</td>
<td>0.03</td>
</tr>
<tr>
<td>Speed (mm/min)</td>
<td>2</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>3</td>
</tr>
<tr>
<td>AESensitivity</td>
<td>9</td>
</tr>
<tr>
<td>Acquisition Rate</td>
<td>1.0 [Hz]</td>
</tr>
<tr>
<td>Type of indenter</td>
<td>Sphero-conical diamond</td>
</tr>
<tr>
<td>Serial number</td>
<td>SH-A27</td>
</tr>
<tr>
<td>Material</td>
<td>Diamond</td>
</tr>
<tr>
<td>Radius (µm)</td>
<td>200</td>
</tr>
</tbody>
</table>

Tab 3.2 2nd scratch test parameters

3.4.4 Color measurement:
The variations in samples’ surface color were measured using a Konica Minolta colorimeter. On each sample 10 measures were taken obtaining data on the three parameters needed:
Lightness (L): values go from 0 (black) to 100 (white)
Red-Green (a): positive values refer to red, negative to green, 0 means neutral.
Yellow-Blue (b): positive values refer to yellow, negative to blue, 0 is neutral
So the average value of L, a and b were taken and $\Delta E$ was computed

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

The unaged samples values were taken as reference.
4. Results and discussion

4.1 Case studies

4.1.2 Colorimeter

The assessment of chromatic variation is quite representative of the degradation status of an object.

*Telegono lamp*

The measurements were carried out on the external body, the internal part and under the base of the red part (fig. 4.1) giving these results (Tab 4.1):

<table>
<thead>
<tr>
<th>Position</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal</td>
<td>39.93</td>
<td>44.98</td>
<td>27.53</td>
</tr>
<tr>
<td>External</td>
<td>41.13</td>
<td>49.26</td>
<td>32.64</td>
</tr>
<tr>
<td>Under the base</td>
<td>43.05</td>
<td>52.52</td>
<td>35.10</td>
</tr>
</tbody>
</table>

*Tab 4.1 Colorimetric analysis results for Telegono*

As previously said, yellowing and discolouration are some of the most evident consequences of photo oxidation; since the colorimetric analyses were carried out on a red surface, it is hard to evaluate a progress in yellowing so it’s better to focus on red discolouration. The value of a* is a measure of red index and, from tab 4.1 results lower for the internal surface and higher for the area under the base. Also L* seemed to follow the same trend of a* probably because the internal zone is the one more exposed to bulb’s light. It can be concluded that the most degraded area of “Telegono” body is the internal one.
KD 4335 lamp

Measures on the body of KD lamp were done comparing the external area and the internal one, probably in contact with the light globe.

<table>
<thead>
<tr>
<th>Position</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal</td>
<td>84.14</td>
<td>-1.10</td>
<td>15.17</td>
</tr>
<tr>
<td>External</td>
<td>85.71</td>
<td>-0.43</td>
<td>20.11</td>
</tr>
</tbody>
</table>

In this case the more degraded part seems to be the external one; this is observable looking at the increasing value in the b* coordinate. A possible explanation could be that the internal part, which is close to the light bulb, were subjected to thermal degradation, while
the external part, more exposed to solar light were degraded due to photo oxidation. Since it’s difficult to establish if, and how long, this lamp has been used, from colorimetric results (in particular b* value) it was supposed that the major cause of degradation was photo oxidation; moreover, from web researches it was find out that between the internal part and the bulb there was a light globe which probably behaved as a sort of protection.

4.1.3 Stereo microscope
Microsamples of Telegono and KD 3445 lamp were examined using a stereomicroscope. This analysis made evident the differences between exposed and non-exposed parts of the lamp.

**Telegono lamp**
Three representative examples are proposed in fig 4.3

Fig 4.3 Samples from “Telegono” observed with stereo microscope and the corresponding area from which they come from

Pictures a,d and g refers to the exposed areas, the pictures b, e and h show the internal side of such samples while the pictures on the right show the localization of samples.
Sample of figure (a) was taken from the side crack of the red ABS body next to the place where the bulb is screwed.
Sample of figure (d) belong to the PP made light globe, while sample (g) was taken from the ABS made compartment.

Comparing pictures (g) and (h) is evident a net contrast in the color; the yellowing due to photo oxidation of the compartments is visible also to the naked eye, moreover the presence of several cracks on the more degraded side can be observed.

Looking at pictures (d) and (e) is observable a difference in the lightness and the presence of dark particles.

The differences in (a) and (b) can be seen in the contrast between the compact surface of the picture on the left against the rugged surface on the right and, again, the presence of dark particles. This is probably due to the fact that, even if the picture on the right refers to the internal side, the sampling area corresponds to a big crack (c) which had allowed the accumulation of powders and dust.

KD 3445 lamp

A comparison between the two sides of a micro sample cut from the external surface of KD lamp is shown.

![Fig 4.4 Samples from the external surface of "KD 4335" observed with a stereo microscope](image)

The difference between the external and non internal sample surfaces is evident. The same kind of comparison is showed also for a sample coming from the external surface of the lamp.
It is also visible that the yellowing of samples in fig 4.5 is less evident with respect to the sample of fig 4.4, according to data of colorimetric analyses.

4.1.5 SEM

Picture of a sample from the red body of Telefono lamp, using QBSD detector at a magnification 1000 is shown in fig4.6. The rugged surface is visible and the white points were identified as Ba, the bigger ones, and Cd, as showed in the following picture, probably belonging to red pigment. Synthetic cadmium pigments based on cadmium sulphide, indeed, are valued for their good thermal stability, light and weather fastness, chemical resistance and high opacity, moreover it has a wide commercial spread. [23]
4.1.6 FTIR

Telegono lamp

The aim of this analysis was to identify the base materials the object is made of and the assessment of its conservation conditions. ABS resulted the constituent material for the body and the compartments of Telegono lamp, while the light globe resulted made in PP.

A first comparison was made between the internal part of the red body, the one more exposed to light (red spectrum), and the external surface (blue spectrum).

The two spectra were normalized considering that the C≡N bond (2238 cm⁻¹) doesn’t change during degradation and so fixing an equal value of absorbance.
The peak at 1721 cm\(^{-1}\) is diagnostic for the carbonyl stretching of an ester group. The ester may be present as additive in the ABS formulation which could be a heat stabilizer belonging to the class of sterically hindered phenolic antioxidants. This is also a characteristic peak of degraded ABS due to the oxidation process.

The other peak that definitely refers to a degradation state is the one at 3440 cm\(^{-1}\) typical of O-H bond.
Fig 4.9 shows that both the internal and the external surface seem degraded in fact in both cases peaks at 3440 cm\(^{-1}\) and 1721 cm\(^{-1}\) are evident. Moreover a difference on the degradation level is deducible: the surface more exposed to the bulb light has higher OH and C=O peak intensity, pointing out a higher level of degradation. Furthermore the reduction in the intensity of peaks at 913 cm\(^{-1}\) and 967 cm\(^{-1}\) are, in the same way, diagnostic of degradation.

This result matches with the colorimetric one, by which was evident that the photo degradation was higher for the surface more exposed to artificial light.

The characteristic peaks referred to ABS polymer are (Tab 4.3):

<table>
<thead>
<tr>
<th>Peak/ cm(^{-1})</th>
<th>Attribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>758</td>
<td>ω S CH(_2) ring bends</td>
</tr>
<tr>
<td>911</td>
<td>ω - CH 1,2 PB</td>
</tr>
<tr>
<td>966</td>
<td>ω - CH 1,4 PB</td>
</tr>
<tr>
<td>1071</td>
<td>ν - PS ring modes</td>
</tr>
<tr>
<td>1156</td>
<td>ν - PS ring modes</td>
</tr>
<tr>
<td>1181</td>
<td>ν - PS ring modes</td>
</tr>
<tr>
<td>1355</td>
<td>ω - CH 1,2 PB and 1,4 PB</td>
</tr>
<tr>
<td>1453</td>
<td>δ(_s) - CH(_2) scissoring</td>
</tr>
<tr>
<td>1494</td>
<td>ν(_s) - PS ring modes</td>
</tr>
<tr>
<td>1583</td>
<td>ν - PS ring modes</td>
</tr>
<tr>
<td>1602</td>
<td>ν - PS ring modes</td>
</tr>
<tr>
<td>1639</td>
<td>ν - CH 1,2 PB</td>
</tr>
<tr>
<td>2237</td>
<td>ν(_s) - CN</td>
</tr>
<tr>
<td>2800-3000</td>
<td>ν(_s), ν(_as) - Aliphatic CH stretching</td>
</tr>
<tr>
<td>3000-3200</td>
<td>ν(_as) Aromatic CH stretching</td>
</tr>
</tbody>
</table>

*Tab 4.3 ABS IR characteristic peaks*
Figure 4.10 is relative to the compartments of Telegono lamp. It shows a comparison between the spectrum of the external sample and the spectrum of a sample taken from a deeper area, and then resulting non degraded.

The red line correspond to the external sample while the purple one refers to the interior sample.

The characteristic peaks relative to degradation are evident (3406 cm\(^{-1}\) and 1720 cm\(^{-1}\)). Moreover a reduction in the peaks at 911 cm\(^{-1}\) and 966 cm\(^{-1}\) relatives to CH bonds is visible due to the photolysis of the methylene bond in the trans-1,4-polybutadiene structure that produce an allylic radical polymer chain.

An infra red spectrum was achieved also for the light globe, finding out that Polypropylene is the constituent polymer. As done for the ABS parts, a comparison was made between the internal (red line) and the external part (blue line).
Here the characteristic peaks of PP (Tab. 4.4):

<table>
<thead>
<tr>
<th>Peak/ cm⁻¹</th>
<th>Attribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>2958</td>
<td>ν (stretching) CH₃</td>
</tr>
<tr>
<td>2885</td>
<td>ν CH₃</td>
</tr>
<tr>
<td>2838</td>
<td>ν CH₂</td>
</tr>
<tr>
<td>1461</td>
<td>δ (symm bending vibration) CH₂</td>
</tr>
<tr>
<td>1380</td>
<td>δ CH₃</td>
</tr>
<tr>
<td>1165</td>
<td>Isotactic band</td>
</tr>
<tr>
<td>997</td>
<td>Isotactic band</td>
</tr>
<tr>
<td>977</td>
<td>Isotactic band</td>
</tr>
</tbody>
</table>

*Tab. 4.4 PP IR characteristic peaks*

The obtained spectra are saturated and so it’s hard to draw satisfying conclusions. It can be considered that degradation of polypropylene mostly affect the tertiary hydrogen that is the more labile, the reduction in intensity of peaks at 2839, 2868, 1377 and 1456 cm⁻¹ could be explained with a loss in the amount of CH₃.

**KD 3445**

Similar analyses were carried out also for the KD lamp.
A comparison between the exposed area of the internal surface (red spectrum) and a deeper sample which is also taken from the internal surface (blue spectrum), was carried out. (fig 4.12).

The peaks relative to degradation, at 3400 cm\(^{-1}\) and 1724 cm\(^{-1}\) are much higher for the exposed area with respect to the deeper sample. As seen for Telegono lamp, is observable a reduction in peaks at 912 cm\(^{-1}\) and 960 cm\(^{-1}\) for the exposed area, typical of a decreasing value in CH bond amount.

Looking at spectra obtained from Telegono’s lamp body and KD 4335 it can be seen that a further peak, not strictly belonging to ABS spectrum, at 3300 cm\(^{-1}\) is present.

In order to identify this peak extraction tests have been done, while Py GC-MS analysis are in progress.

The extractions were carried out using different solvents:

- Tetrahydrofuran (THF)
- Dichloromethane (CH\(_2\)Cl\(_2\))
- Chloroform (CHCl\(_3\))
- Hexane
- Dimethylformamide (DMF)
- Benzene
The aim of this analysis was to find a suitable solvent for the ABS polymer in order to separate the polymer and the additive. Solubility results are shown in tab 4.5.

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>SOLUBILITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>no</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>partial</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>partial</td>
</tr>
<tr>
<td>DMF</td>
<td>partial</td>
</tr>
<tr>
<td>Benzene</td>
<td>no</td>
</tr>
<tr>
<td>THF</td>
<td>total</td>
</tr>
</tbody>
</table>

Tab 4.5 Solubility test results

The extraction in CH₂Cl₂ and CHCl₃ lead to a better solubility with respect to hexane but, in both cases, suspended particles were present. In a first step we tried to filter the solution in order to separate liquid from solid but it turned out to be difficult so, for chloroform solution, dichloromethane, and DMF, the liquid part composed by solvent and suspensions, was taken with a pipette and analyzed. (fig 4.13, 4.14, 4.15)

![Fig 4.13 FTIR spectrum of red "Telegono" ABS and dichloromethane solution](image)

All the peaks refers to ABS spectrum, except for the one at 1265 cm⁻² that is typical of dichloromethane.
Also in this case all the peaks are characteristic of ABS except for the ones at $1212 \text{ cm}^{-1}$ and $670 \text{ cm}^{-1}$ typical of CHCl$_3$. We can notice that the peak at $760 \text{ cm}^{-1}$ is much higher with respect to the previous case, because the ABS peak is added to the chloroform one. In both cases features typical of degraded ABS are not present because the sample was taken from a depth area of the red body taking advantage of the crack on the red body’s side.

Peaks typical of DMF are at $1384 \text{ cm}^{-1}$, $1687 \text{ cm}^{-1}$, $1086 \text{ cm}^{-1}$, the remaining peaks belong to the ABS spectrum. None of these resulting spectra was helpful in determining the $3300 \text{ cm}^{-1}$ peak.
The extraction in THF gave good results in terms of solubility; after observing a quasi total dissolution of ABS, we made the solid part to coagulate adding the solution to a higher amount of ethanol. Afterwards the new solution was filtered and both the liquid part and the solid part were analyzed. In fig 4.16 the comparison between the solid polymer (violet spectrum) and the solvent (red spectrum) can be seen.

Using OMNIC software and literature it was found out that the peak at 3300 cm\(^{-1}\) may correspond to a N-H bond. It was supposed that the NH bond could belong to an amine compounds, indeed amines have been frequently used as light stabilizers and to prevent thermal degradation in polymer blends.

GC-MS analysis is in progress in order to support this hypothesis.
4.2 Standard plastics

In this section the results of characterization analyses are sorted by material.

4.2.1 Polyvinylchloride (PVC)

A qualitative picture showing PVC specimens at each aging time is reported in Fig 4.17.

![Aged PVC, comparison between aging time](image)

**Colorimetric analysis**

Colorimetric measurements have been made on each sample. The yellowing increase, visible at a first macro observation (Fig 4.17) was confirmed by the analysis (Tab 4.6).

<table>
<thead>
<tr>
<th>Time of ageing</th>
<th>L*</th>
<th>A*</th>
<th>B*</th>
<th>ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 h</td>
<td>92,1</td>
<td>-1,1</td>
<td>7,5</td>
<td>0</td>
</tr>
<tr>
<td>100 h</td>
<td>92,3</td>
<td>-0,7</td>
<td>5,5</td>
<td>2,1</td>
</tr>
<tr>
<td>250 h</td>
<td>91,9</td>
<td>-0,9</td>
<td>7,1</td>
<td>0,5</td>
</tr>
<tr>
<td>500 h</td>
<td>85,6</td>
<td>1,0</td>
<td>19,6</td>
<td>13,9</td>
</tr>
<tr>
<td>700 h</td>
<td>78,5</td>
<td>4,6</td>
<td>25,9</td>
<td>23,6</td>
</tr>
</tbody>
</table>

*Tab 4.6 PVC Colorimetric analysis results*
Chapter 4 Results and Discussion

The visible consequences of degradation on the samples’ surface are, as already said in chapter 2, a change in color from white to brown - yellow for higher level of degradation. This can be explained by the growing polyene sequences resulting from the dehydrochlorination [15]. As $b^*$ parameter’s values increase, it is expected a corresponding decrease in lightness, moreover the increasing in “b” values together with the decreasing in “L” values should be proportional to the level of aging.

The results obtained by the colorimetric analysis confirmed this expectation as reported in Tab 4.6 and Fig 4.18, except for the values achieved on the 100 hours aged sample. This sample resulted to be less yellow than the unaged one and with a comparable lightness value; a possible explanation could lie in the presence of an original covering material that fade away in the early stage of degradation revealing a less degraded surface.

**Microscopic observation**

Samples at each stage of degradation have been observed with a stereo microscope. Maintaining constant the parameters, as exposition, gain, saturation, position and intensity of lights used, a comparison between the taken pictures has been obtained, as reported in Fig 4.19 and 4.20. As it can be noticed from the lower magnification (2 mm) the change in color can be observed. On the sample aged up to 500 hours, initial signs of yellowing was visible, not as a uniform color, but as high transparency yellow stains. The 700 hours aged sample, a yellowing in the form of dense pitting can be noted.

The yellow pitting formation result more evident at 200 µm (Fig. 4.20)
From this first magnification (2 mm) the change in color can be observed. On the sample aged up to 500 hours, initial signs of yellowing was visible, not as a uniform color, but as high transparency yellow stains. The 700 hours aged sample, a yellowing in the form of dense pitting can be noted. The yellow pitting formation result more evident at 200 µm (Fig. 4.20)
FTIR analysis
Attenuated Total Reflectance (ATR) has been used to study the degradation of aged PVC in time.
Wavenumber [cm$^{-1}$] | Attribution | Band character
--- | --- | ---
2967 | CH$_2$ | weak
2919 | CH | strong
2850 | CH$_2$ | medium
2818 | CH | weak
1435 | C-H amorphous | medium
1425 | C-H crystalline | strong
1332 | C-H twist | medium
1254 | H-C-Cl bend | strong
961 | C-H rock | medium
692 | C-Cl | weak
682 | C-Cl | medium
668 | C-Cl | strong

Tab 4.7 PVC IR characteristic peaks

From literature data it was found that the obtained spectrum is comparable with one relative to PVC with the presence of CaCO$_3$ and DOP (dioctyl phthalate) used, respectively, as filler and plasticizer. [14]

A scheme of the characteristic peaks for CaCO$_3$ and DOP are reported in Tab 4.8:

<table>
<thead>
<tr>
<th>DOP</th>
<th>CaCO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wavenumber (cm$^{-1}$)</strong></td>
<td><strong>Attribution</strong></td>
</tr>
<tr>
<td>2960</td>
<td>CH$_3$CH$_2$</td>
</tr>
<tr>
<td>2873</td>
<td>CH$_3$CH$_2$</td>
</tr>
<tr>
<td>1727</td>
<td>C=O</td>
</tr>
<tr>
<td>1600</td>
<td>Aromatic ring</td>
</tr>
<tr>
<td>1461</td>
<td>Comb. CH$_3$ + CH$_2$</td>
</tr>
<tr>
<td>1125</td>
<td>C-O</td>
</tr>
<tr>
<td>1075</td>
<td>=C-H</td>
</tr>
<tr>
<td>1040</td>
<td>O(CH$_2$)$_2$</td>
</tr>
<tr>
<td>743</td>
<td>=C-H</td>
</tr>
</tbody>
</table>

Tab 4.8 DOP and CaCO$_3$ IR characteristic peaks

Gas chromatography mass spectrometry (GC-MS) analyses are in progress aimed at supporting the hypothesis that DOP was the used plasticizer.
In Fig 4.22 the comparison between different stages of degradation for PVC samples is shown;
Red spectrum refers to 700 hours of aging, the blue one to 500 hours, the purple to 250 hours, the orange to 100 hours and the green one is the unaged sample.

![Fig 4.22 ATR spectrum of aged PVC (red spectrum refers to 700h, blue to 500h, purple to 250h, orange to 100h, green to 0h)](image)

The spectra were normalized on the peak at 1330 cm\(^{-1}\) which is attributed to the C-H twist and is considered not to change with degradation. [15]

Observing the spectra, several diagnostic degradation signs can be noticed. The most evident is the band around 3400 cm\(^{-1}\), typical of the O-H formation: as already said, during photooxidative degradation, the hydrogen abstraction from the polymer backbone can lead to the formation of alkyl radicals; the reaction of these radicals with molecular oxygen leads to peroxy radicals. Hydroperoxides are then formed and can be detected by their absorption in the region between 3400 and 3300 cm\(^{-1}\).

The presence of CaCO\(_3\) in the PVC blend, lead to the formation, during degradation, of CaCl\(_2\) detectable by the peak around 1630 cm\(^{-1}\). As consequence, to the increasing in CaCl\(_2\) amount corresponds a consequently decreasing in CaCO\(_3\) concentration as visible from the peak at 876 cm\(^{-1}\). Moreover, the main mechanism of photooxidative degradation is the formation of conjugated polyene chains resulting from the hydrochlorination. Double bonds C=C absorption in the IR spectrum is around 1630 cm\(^{-1}\) as well, explaining the evident increase in the intensity of such peak.

The break of H-C-Cl bonds results in a reduction of 1254 cm\(^{-1}\) peak intensity, while the breaks of C-H bonds is visible in the reduction of peaks at 1425 and 961 cm\(^{-1}\).
In fig 4.23 a reduction of peak at 1730 cm\(^{-1}\) is visible, which is the consequence of the plasticizer flowing out with the degradation time. fig 4.24 and fig 4.25 show that the reduction in DOP is slow in the first stages of degradation becoming faster as the time of exposition increase and in agreement with literature data (fig 4.25) [5].
Chapter 4 Results and Discussion

**Fig 4.25** Variation in DOP concentration in PVC samples exposed to accelerated aging as reported by Mikiya Ito [5]

**SEM Analysis**

**Fig 4.26** SEM analyses on PVC unaged (a) and PVC at 700 hours (b). For both pictures the detector is QBSD

**Fig 4.27** SEM analyses on PVC unaged (c) and PVC at 700 hours (d). For both pictures the detector is VPSE
Comparing Figures 4.27.c and 4.27.d it is evident that the surface of PVC aged at 700 hours is more rough. The two images in back scattered mode, 4.26.a and 4.26.b, show some evidence about the amount of CaCO₃. The white spots visible in both pictures, indeed, represent the concentration of calcium carbonate, as confirmed by the map of fig4.28. It’s not possible to detect changes in CaCO₃ concentration as a consequence of aging because its product of degradation (CaCl₂) contains Calcium as well.

**Scratch test**
Scratch test results are shown in the following figures. As expected, the depth at which the indenter scratches the surface, increases with the load applied, but in each case is evident from the results that the depth doesn’t increase monotonically with the aging time (fig 4.30).
The unaged specimen always corresponds to the higher depth, while lower levels of depth were achieved with the more degraded specimens. It can be deduced that, as the aging time increase, on equal terms, the polymer become harder and stiffer so the tip penetration resulted more difficult. Moreover, looking at fig 4.32 it can be seen that, at each applied load, Pd followed the same trend.
The apparent friction, calculated as the ratio between $F_t$ and $F_n$, results from two components, the adhesive and deformational one. As the time of aging increases an increasing in friction is visible (fig 4.33 and 4.34) and can be explained referring to both the two components. The deformational components leads to a higher resistance to the cold flow, in agreement with the reduction of $P_d$. One of degradation effects is the increase in stiffness so that a reduction in the friction coefficient should be expected. However, the aging phenomenon changes the surfaces characteristics modifying the interaction with the tip so, a possible explanation of what is shown in fig 4.33, could be the formation of a sticker surface.
In the 2nd set a spher-conical diamond indenter has been chosen. (Fig 4.35)
As already said, this kind of tip was chosen so that a high damaging situation could be achieved. Effectively, local decay phenomena can be observed, supported by the formation of micro cracks, probably due to material embrittlement which couldn’t be detected in the first set of test conditions.
Looking at fig 4.35, the following qualitative conclusions can be drawn.
The big difference between the two samples is in the shape of the Pd curve (fig 4.35). In the case of the unaged sample, the tip moves creating a unique and homogeneous scratch, while in the second case (700 hours of aging) a discontinue scratch could be observed, leading to a sinusoidal variation of Pd.

This is evident also from the microscopic observation shown in fig 4.36, where the formation of little grooves on the scratch profile of the aged specimen is clearly visible.
4.2.2 Acrylonitrile Butadiene Styrene (ABS)

**Microscopic Observation**

![Image of stereo microscope pictures of ABS unaged at 100h (a), 250h (b), 500h (c), 1000h (d), 1000h (e)]

*Fig 4.36 Stereo microscope pictures of ABS unaged (a) at 100h (b), 250h (c), 500h (d), 1000h (e)*

Picture of exposed areas of aged ABS observed with stereo microscope are reported in picture 4.37.

No evident differences on surface morphology have been detected, apart for the change in color, the typical yellowing of ABS degradation.
**Colorimetric analysis**

Results of colorimetric analysis showed an increase in “b” values in time (fig 4.38 and Tab 4.9Tab 4.9) and a reduction in lightness. These results confirmed what was visible with microscopic observation, the yellowing as consequence of photo oxidation, increases with the aging time.

<table>
<thead>
<tr>
<th>Time of ageing</th>
<th>L</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>0h</td>
<td>85.6</td>
<td>-3.2</td>
<td>8.4</td>
</tr>
<tr>
<td>100h</td>
<td>83.7</td>
<td>-3.8</td>
<td>17.5</td>
</tr>
<tr>
<td>250h</td>
<td>82.4</td>
<td>-3.3</td>
<td>22.2</td>
</tr>
<tr>
<td>500h</td>
<td>79.1</td>
<td>-0.5</td>
<td>28.4</td>
</tr>
<tr>
<td>1000h</td>
<td>74.5</td>
<td>1.8</td>
<td>30.5</td>
</tr>
</tbody>
</table>

*Tab 4.9 ABS Colorimetric analysis results*

**SEM analysis**

SEM micrographs are reported in Fig4.39, showing morphological variations that were invisible at the Stereo microscope. With the comparison between unaged ABS specimen and after 1000h of accelerated aging, the formation of randomly oriented micro cracks can be noticed.
**FTIR analysis**

Each ABS specimen, aged at 0h, 100h, 250h 500h and 1000h, was analyzed by means ATR spectroscopy and a comparison between spectra obtained at different aging time was achieved.

The degradation of ABS following photo-irradiation was evident in the reduction of double bonds in 911 cm\(^{-1}\) (1,2-PB) as well as in 967 cm\(^{-1}\) peak from the trans-1,4-PB functional group and formation of hydroxyl and carbonyl groups.[17]

A visible increasing in the intensity of peak at 1721 cm\(^{-1}\) can be noticed (Fig 4.40). This is one of the characteristic peaks of carbonyl compounds (ester, aldehyde or ketone for example), and represent a clear sign of degradation since it refers to the growing amount of oxidation products during degradation.

The blue spectrum refers to 700 hours of aging, violet to 500 hours, light blue to 250 hours, orange to 100 hours and the red one represents the unaged specimen.
Fig 4.39 Detail of ATR spectra for aged ABS at different ageing time. Peak at 1721 refers to carbonyl compounds formation.

**Scratch test**

The scratch test was carried out following the second set of parameters (sphero-conical diamond indenter).
Scratch test results, fig 4.41a showed a behaviour similar to PVC. Penetration depth values appear lower with respect to the unaged specimen confirming what already said in chapter 2: degradation lead to a brittle and stiffer material and increased the hardness. This is visible also from microscopic observation of scratch profile in fig 4.41b; where the tip start to scratch the specimen, radial micro cracks can be noticed (on the right) as well as the production, during the test, of lots of chips.
4.2.3 Polypropylene (PP)

*Microscopic observation*

According to Schoolemberg [19] between 250 and 300 hours of aging (using a Xenon lamp) cracks become visible on the surface until, after 1000 h, a completely crumbled and powdery surface is reached. The surface cracked spontaneously, even without a mechanical input, and these cracks are randomly oriented.

Fig 4.42 shows the initial growth of cracks that can be seen starting from 250 hours, appearing as parallel cracks. After 500 h of ageing cracks density and cracks length increase, still oriented in a unique direction. When 1000 h of aging are reached cracks appeared also perpendicular to the previous and their density is increased.

*Fig 4.41 Aged PP observed with stereo microscope after 100h (a), 250h (b), 500h (c) and 1000h (d)*
SEM analysis

A confirmation of what already visible with microscopic observation was given by the SEM micrographs in Fig.4.43 showing the formation of microcracks strongly evident and marked.

![SEM micrographs of unaged and aged PP. Detector: VPSE](image-url)
**Chapter 4 Results and Discussion**

## Colorimetric analysis

<table>
<thead>
<tr>
<th>Time of aging</th>
<th>L</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>0h</td>
<td>65,1</td>
<td>1,5</td>
<td>1,2</td>
</tr>
<tr>
<td>100h</td>
<td>66,6</td>
<td>0,9</td>
<td>3,5</td>
</tr>
<tr>
<td>250h</td>
<td>66,8</td>
<td>-0,1</td>
<td>5,6</td>
</tr>
<tr>
<td>500h</td>
<td>65,7</td>
<td>-0,5</td>
<td>7,5</td>
</tr>
<tr>
<td>1000h</td>
<td>65,7</td>
<td>-0,5</td>
<td>6,7</td>
</tr>
</tbody>
</table>

*Tab 4.10 PP Colorimetric analysis results*

![Colorimetric results for aged PP](image)

Results for colorimetric analyses are shown in fig 4.44 and Tab 4.10. The yellowing effect, as consequence of degradation, is typical of Polypropylene too and was confirmed by the results. Lightness results, on the other hand, were not the expected outcome; indeed L values seemed to increase as the aging proceeded until 500h were reached. At that point a marked increase in yellowness is reached which, also, corresponds to a reduction in lightness.
FTIR analysis

For peaks identification tab 4.4 can be used. According to Tidjani [20], the photo-oxidation of Polypropylene lead to the formation of photo products, the most can be seen in the carbonyl region, from 1700 to 1800 cm\(^{-1}\) where several shoulders and bands formed after degradation, attributed to ester, perester, \(\gamma\)-lactone entities.

The appearance and growth of 1733 cm\(^{-1}\) peak, visible in fig 4.45b and 4.45c, confirm the previous statement. The comparison between spectra obtained at each aging time was achieved normalizing on the 1456 cm\(^{-1}\) peak, characteristic of methylene group, since it was considered not to change during degradation.

During degradation PP usually undergo to chain scission; the dissociation of C-H bonds result in the formation of secondary and tertiary alkyl radicals which, after combination with oxygen followed by hydrogen abstraction from the polymer chain, generate secondary and tertiary hydroperoxides [20]. These hydroperoxides absorb in the IR in the region between 1250 and 1300 cm\(^{-1}\), as observable in fig 4.45b. It is also evident from fig 4.45a that both carbonyl groups and hydroperoxides weren’t present in the unaged sample.

Moreover, a reduction in the 1277 and 2723 cm\(^{-1}\) intensity can be seen, characteristic peaks of methyl group and C-H bonds, due to chain scission.

![Fig 4.44.a ATR spectrum of unaged PP](image-url)
Chapter 4 Results and Discussion

![ATR spectra of aged PP](image)

**Fig 4.45.b** ATR spectra of aged PP

![ATR spectra of aged PP, zoom on 1733 cm⁻¹ peak](image)

**Fig 4.45.c** ATR spectra of aged PP, zoom on 1733 cm⁻¹ peak
Scratch test

The depth of scratch was plotted against the scratch length (fig 4.46), it can be noticed that, at 10N, as well as at 25 N, PP unaged had higher resistance to scratch with respect to the aged sample. Moreover, it is observable that, for the unaged specimens, the obtained curves were perfectly comparable while it was not true for aged specimens. This behavior can be attributed to a loss in ductility and to an increase in chips production that probably interfere with the indenter.

Scratch test results (fig 4.46) supported by a microscopic observation (fig 4.47) and SEM micrographs of fig 4.43, underlighted, once again, the clear embrittlement phenomenon. The aging, combined with scratch, lead to several damaging consequences as cracks formation and material asporation which result in higher values of depth.
4.2.4. High-density Polyethylene (HDPE)

*Colorimetric analysis*

<table>
<thead>
<tr>
<th>Time of aging</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0h</td>
<td>78,4</td>
<td>-2,0</td>
<td>-2,7</td>
</tr>
<tr>
<td>100h</td>
<td>77,6</td>
<td>-2,2</td>
<td>-0,6</td>
</tr>
<tr>
<td>250h</td>
<td>77,0</td>
<td>-2,1</td>
<td>0,6</td>
</tr>
<tr>
<td>500h</td>
<td>76,4</td>
<td>-1,9</td>
<td>1,6</td>
</tr>
<tr>
<td>1000h</td>
<td>75,1</td>
<td>-1,3</td>
<td>2,7</td>
</tr>
</tbody>
</table>

*Fig 4.47 Colorimetric analysis on aged HDPE*

Results of colorimetric analyses are shown in fig4.48 and Tab 4.11. During degradation the b* value increases proportionally with the ageing time. As for ABS and PVC case, to higher values of b, correspond lower L values.
Microscopic observation

What is clearly visible with colorimetric analyses result difficult to be seen at the stereo microscope observation (fig 4.49). Few changes, both in color and surface morphology which appear rougher, have been detected.

FTIR analysis

Degradation of Polyethylene leads to the formation of photo products (esters, carboxylic acid groups, γ-lactones) detectable with FTIR spectroscopy in the formation of carbonyl bands, around 1700 cm\(^{-1}\). The ratio between the typical peaks of PE (1473 cm\(^{-1}\)) and the intensity of carbonyl peaks, in this case at 1714 cm\(^{-1}\), gives an acceptable measure of photo oxidation degree.

Indeed tab 4.12 show what was expected, the ratio would decrease with aging time. Moreover, as also visible from the particular of fig 4.50b, the spectra of 100h and 250h, for what concern the 1714 cm\(^{-1}\) intensity, are comparable.

<table>
<thead>
<tr>
<th>AGING TIME</th>
<th>1473 cm(^{-1})/1714 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>100h</td>
<td>15,3</td>
</tr>
<tr>
<td>250h</td>
<td>15,8</td>
</tr>
<tr>
<td>500h</td>
<td>7,55</td>
</tr>
<tr>
<td>1000h</td>
<td>5,93</td>
</tr>
</tbody>
</table>

Tab 4.12 Ratio between 1473 cm\(^{-1}\) and 1714 cm\(^{-1}\) intensity for HDPE

Resulting spectra can be seen in fig 4.50a and 4.50b
Chapter 4 Results and Discussion

Fig 4.49a ATR spectra of aged HDP. Comparison between unaged sample (violet), 100h (purple), 250h (green), 500h (light blue) 1000h (red)

Fig 4.50b

<table>
<thead>
<tr>
<th>Wave number [cm⁻¹]</th>
<th>Attribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>2919</td>
<td>CH₂ asymmetric stretching</td>
</tr>
<tr>
<td>2851</td>
<td>CH₂ symmetric stretching</td>
</tr>
<tr>
<td>1473, 1463</td>
<td>Bending deformation</td>
</tr>
<tr>
<td>1377</td>
<td>CH₃ symmetric deformation</td>
</tr>
<tr>
<td>1366, 1351</td>
<td>Wagging deformation</td>
</tr>
<tr>
<td>1306</td>
<td>Twisting deformation</td>
</tr>
<tr>
<td>1176</td>
<td>Wagging deformation</td>
</tr>
<tr>
<td>731-720</td>
<td>Rocking deformation</td>
</tr>
</tbody>
</table>

Tab 4.13 PE IR characteristic peaks
Scratch test

From the scratch test results, fig4.51, it can be stated that the effect of degradation on HDPE mechanical properties consists of a reduction in the mechanical resistance. This is explained by the increasing in scratch depth visible from the curve corresponding to the aged sample.

What can be achieved, also looking at fig4.52, is that the aged HDPE became more brittle; debris that are evident in the aged sample are completely absent in the original sample.
4.2.5 Linear low-density Polyethylene

*Colorimetric analysis*

<table>
<thead>
<tr>
<th>Time of aging</th>
<th>L*</th>
<th>A*</th>
<th>B*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0h</td>
<td>68,1</td>
<td>-1,1</td>
<td>-6,6</td>
</tr>
<tr>
<td>100h</td>
<td>68,5</td>
<td>-0,9</td>
<td>-5,0</td>
</tr>
<tr>
<td>250h</td>
<td>68,4</td>
<td>-1,0</td>
<td>-4,7</td>
</tr>
<tr>
<td>500h</td>
<td>68,2</td>
<td>-1,0</td>
<td>-4,7</td>
</tr>
<tr>
<td>1000h</td>
<td>68,3</td>
<td>-0,8</td>
<td>-5,0</td>
</tr>
</tbody>
</table>

*Tab 4.14 LLDPE Colorimetric analysis results*

*Fig 4.52 Colorimetric results of Linear low-density polyethylene*

Colorimetric analyses (tab 4.14 and fig 4.53) showed that a minimal variation can be seen for lightness, while, for *b* value, the major variation is achieved between 0 and 100 hours, afterwards, the results oscillate around a similar new value.
Microscopic observation

Fig 4.53 Stereo microscope pictures of unaged LLDPE (left) and after 1000h (right)

Fig 4.54 shows the pictures taken with stereo microscope, underlining that no visible variations are present, as confirmed by the colorimetric analyses.

FTIR analysis

For peak’s wavenumbers, tab 4.13 can be used.

Concerning FTIR spectroscopy, similar results to HDPE could have been expected, but looking at fig 4.55, no significant variation in each aged time can be observed, nor the formation of bands in the carbonyl region. These results agreed with the ones obtained from the previous characterization analyses.
**Scratch test**

The few changes during degradation founded with LLDPE are confirmed also by the scratch test (fig 4.56). This is explained considering that LLDPE is much more ductile with respect to the other semi crystalline polymers tested before. Further tests, varying the indenter type could provide further information, getting close to more severe conditions in order to induce fractures in the material. Moreover, it could be interesting to submit the unaged samples to further characterization analyses in order to detect the additives present in the blend and justify the obtained results.

![Scratch depth against scratch length for unaged and 1000h LLDPE](image)

**Fig 4.55 Scratch depth against scratch length for unaged and 1000h LLDPE**

### 4.2.6 Comparison between case studies and standard material

A comparison between the degradation progress of ABS and PP specimens and the most significant parts of case studies was carried out. The selected areas are “Telegono” compartments and light globe, made of ABS and PP respectively, and the “KD 4335” shell made of ABS. These two lamps were manufactured in the same period of time, indeed “Telegono” can be dated in 1968 and “KD 43335” in 1965, so a similar degraded condition could be expected. However the exposition condition and of use may have been significantly different leading to a different aging.
ABS

Starting with ABS, the artificially aged specimens were compared to the shell of “KD 4335” lamp and to the compartments of “Telegono” lamp, both made of ABS. The confrontation is based on FTIR spectroscopy and colorimetric analyses results. In fig 4.57 the comparison between aged ABS and “Telegono” compartments is shown, blue spectrum refers to the lamp sample, the red one to 500h, the green to 250h and the yellow one to 100h.

![FTIR spectra comparison between “Telegono” and aged ABS](image1)

The comparison between aged ABS and “KD 4335” can be observed in fig 4.58; yellow spectrum refers to 500h, the red to 100h and the blue one to the lamp sample.

![FTIR spectra comparison between “KD 4335” and aged ABS](image2)
Colorimetric analysis results are reported in tab 4.15 and fig 4.59

<table>
<thead>
<tr>
<th>Time of aging</th>
<th>L</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>0h</td>
<td>85,6</td>
<td>-3,2</td>
<td>8,4</td>
</tr>
<tr>
<td>100h</td>
<td>83,7</td>
<td>-3,8</td>
<td>17,5</td>
</tr>
<tr>
<td>250h</td>
<td>82,4</td>
<td>-3,3</td>
<td>22,2</td>
</tr>
<tr>
<td>500h</td>
<td>79,1</td>
<td>-0,5</td>
<td>28,4</td>
</tr>
<tr>
<td>1000h</td>
<td>74,5</td>
<td>1,8</td>
<td>30,5</td>
</tr>
<tr>
<td>&quot;Telegono&quot;</td>
<td>77,6</td>
<td>2,9</td>
<td>34,3</td>
</tr>
<tr>
<td>&quot;KD&quot;</td>
<td>84,7</td>
<td>-0,4</td>
<td>20,1</td>
</tr>
</tbody>
</table>

Tab 4.15 Colorimetric results for aged ABS, “Telegono” and “KD 4335”

Looking both at colorimetric analysis results (fig 4.59) and spectroscopic analysis results (fig 4.57 and 4.58) it seemed that “Telegono” compartments results more degraded with respect to “KD 4335” shell. Observing the results, for the case of “KD 4335” lamp we can imagine to locate its degradation condition just below that of a 100 hours aged ABS specimen. This hypothesis is confirmed both by colorimetric and spectroscopic analysis.

The “Telegono” compartments, on the other hand, looked more degraded and can be located above 500 hours of artificial aging. Looking at spectroscopic results in fig 4.57, indeed, the intensity of 3440 cm\(^{-1}\) peak is higher than the 500h spectrum, moreover the intensity in 2925 cm\(^{-1}\) peak (CH bonds break) is lower than the 500h one, confirming the higher level of degradation. A further support is given by peaks at 911 cm\(^{-1}\) and 967 cm\(^{-1}\), again CH bonds scission. From fig 4.60, founded in the web, a “Telegono” lamp turned on
can be seen, allowing us to imagine one of its possible utilization, in which the light beam is focused on the compartments. This light globe position could be expected to be frequent, leading the compartments to a more aggressive condition and, indeed, a higher degradation with respect to KD 4335.

**Fig 4.59 “Telegono” lamp turned on**

**PP**

Proceeding with case studies and standard material comparison, we can focus on the Polypropylene globe diffusion of “Telegono” lamp and PP specimens.

**Fig 4.60.a FTIR spectra comparison between “Telegono” and aged PP (red spectrum refers to “Telegono” sample, black to 1000h, yellow to 500h, green to 250h, violet to 100h and the blue one to the unaged specimen)**
Looking at Fig. 4.61, the red spectrum refers to “Telegono” light globe, the black one to 1000h, the yellow to 500h, the green to 250h, the violet to 100h and the blue one to the unaged specimen.

Comparing the colorimetric analysis results in Fig. 4.62, a great difference is visible concerning the lightness; the *b value, on the other hand, is comparable with the one corresponding to the PP specimen aged at 250 hours.
Looking at FTIR spectroscopy results (Fig 4.61) we can see that, for Telegono specimen, a peak around 1700 cm\(^{-1}\) is formed. This peak belongs to the carbonyl region, so it is probably relatives to photo products as well as the peak at 1733 cm\(^{-1}\), visible for PP specimens, even if it is clearly shifted.

As a consequence, it’s difficult to make a realistic comparison between lamp and specimens’ spectra; for this reason further in-depth analyses are mandatory.

On the contrary, results concerning ABS specimens were in line with those achieved using ABS parts of both lamps, thereby specimens represented a good support for the lamps’ conditions investigation.
5. Conservation treatments

In the final part of this work, some preliminary tests have been performed with the purpose of setting up new conservative treatments aiming at reducing the surface yellowing, one of the more evident consequences of photo oxidation. The tests were performed after the accelerated aging and only on the most degraded specimens.

5.1 Post additivation

In order to reduce the surface yellowing, due to degradation, several optical whiteners were used. In one hand it was necessary to find a methodology that allowed the additive to be absorbed by specimens surfaces; in the other hand it was necessary to identify which was the most efficient additive.

The selected optical brighteners to be tested are the following:

- 4,4′-Bis(2-benzoxazolyl)stilbene

\[ \text{Fig 5.1 4,4′-Bis(2-benzoxazolyl)stilbene structure} \]

- 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene

\[ \text{Fig 5.2 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene structure} \]

- Polyethylenimine, 80% ethoxylated solution

\[ \text{Fig 5.3 Polyethylenimine structure} \]
Several preliminary tests have been conducted to define the application procedure in order to maximise the absorption of the additive. It should be considered that, while polyethylenimine was available as viscous liquid, 4,4’-Bis(2-benzoxazolyl)stilbene and 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene were available as powders.

All the tests were performed on several 700h aged PVC samples. They were cleaned with a solution of water and ethanol after each test in order to remove the additive that wasn’t completely absorbed.

**Polyethylenimine**

Polyethylenimine was deposited onto one half of three specimens as it was, and onto another three specimens in a solution with Butyl Stearate used as carrier. In both cases one of the specimen was cleaned after 1 day, another one after 3 days and the remaining ones after 5 days.

**4,4’-Bis(2-benzoxazolyl)stilbene and 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene**

In order to make the 4,4’-Bis(2-benzoxazolyl)stilbene and 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene absorbable, a solution with water and ethanol was prepared (for both cases the solution was composed by 20 ml of water, 20 ml of additive and 4 pipettes of ethanol).

The specimen was immersed for a half in the solution stirred using a magnetic stirrer at room temperature.

To better understand the contribution of water/ethanol solution alone separately by the additive one, a specimen was immersed in a solution only composed of water and ethanol. All the specimens were then dried in stove at 40°C.

Colorimetric analyses and Microscope observation were carried out both on the treated and untreated part of the specimen.

In the following table (Tab 5.1), colorimetric results are shown for the specimens before any treatment (pre-add), for the treated part of the specimen (add) and for the part of the specimens not directly exposed to additive absorption. A difference between the two half of the treated specimen were then achieved.

<table>
<thead>
<tr>
<th>additive</th>
<th>pre-add</th>
<th>add</th>
<th>no add</th>
<th>Δ (no add- add)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene</td>
<td>*L</td>
<td>80</td>
<td>82</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>*a</td>
<td>4</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>*b</td>
<td>25</td>
<td>21</td>
<td>23</td>
</tr>
<tr>
<td>4,4’-Bis(2-benzoxazolyl)stilbene</td>
<td>*L</td>
<td>80,4</td>
<td>83</td>
<td>82,9</td>
</tr>
<tr>
<td></td>
<td>*a</td>
<td>3,4</td>
<td>2,4</td>
<td>2,7</td>
</tr>
<tr>
<td></td>
<td>*b</td>
<td>24</td>
<td>20</td>
<td>20,8</td>
</tr>
</tbody>
</table>

*Tab 5.1 Colorimetric analyses results on PVC treated and untreated*
Fig 5.4 Stereo microscope comparison between PVC not treated (left) and after immersion in water and ethanol (right)
Chapter 5 Conservation treatments

Fig 5.6 FTIR spectra of PVC immersed in the water and ethanol solution (green) and not treated (red)

Fig 5.7 FTIR spectra of PVC immersed in the water and 4,4’-Bis(2-benzoxazolyl)stilbene solution (red) and not treated (violet)
Looking at the colorimetric results obtained by the preliminary tests (Tab 5.1 Colorimetric analyses results on PVC treated and untreated), the most efficient additive was chosen to be 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene, in fact, focusing on *b value, the difference between the untreated half of the specimen and the treated one is higher with respect to the second additive, representing a major reduction in yellowing. Moreover, as can be achieved by the stereo microscope picture, also water and ethanol had good cleaning properties on the PVC surface, in fact a comparable difference in the treated and non treated surface can be seen both for the specimen immersed in water and in additive (fig 5.4, fig 5.5).

For these reasons, three new sessions of experiments were carried out followed by a more detailed characterization.

1. PVC was treated only with water,
2. Agar (gel) was chosen for a cleaning treatment
3. PVC was immersed in a 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene and water solution.

The name “agar” refers to a complex mixture of polysaccharide components, which may be derived from certain genera of the Rhodophyceae group of red sea weeds [21].

Agar, in the form of powder, was mixed with water until a gelatine was obtained, and so a thin layer was deposited on PVC surface. Before characterization the Agar layer must be removed.
Colorimetric analyses results are shown in the following figures (Tab 5.2 Colorimetric analysis results for treated PVC (water, Agar, thiophene)) and Fig 5.9); as the previous case, “no add” stands for the half of the specimens which weren’t treated and “add” for the treated part. ∆E, ∆L and ∆b were achieved as the difference between the untreated and the treated part of the specimen.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>L*(D65)</th>
<th>a*(D65)</th>
<th>b*(D65)</th>
<th>∆E</th>
<th>∆L</th>
<th>∆b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>no add</td>
<td>81.53</td>
<td>3.04</td>
<td>23.41</td>
<td>3.09</td>
<td>1.02</td>
<td>2.91</td>
</tr>
<tr>
<td>add</td>
<td>82.55</td>
<td>2.88</td>
<td>20.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2 Agar 3%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>no add</td>
<td>81.34</td>
<td>3.15</td>
<td>23.87</td>
<td>7.46</td>
<td>4.65</td>
<td>5.62</td>
</tr>
<tr>
<td>add</td>
<td>85.99</td>
<td>1.57</td>
<td>18.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3 Thiophene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>no add</td>
<td>80.05</td>
<td>3.8</td>
<td>24.4</td>
<td>1.83</td>
<td>0.87</td>
<td>1.56</td>
</tr>
<tr>
<td>add</td>
<td>80.92</td>
<td>3.41</td>
<td>22.84</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Tab 5.2 Colorimetric analysis results for treated PVC (water, Agar, thiophene)*

The results suggest that the Agar gel is the more effective cleaning procedure; this is confirmed also by the Stereo microscope observation. (fig 5.10, 5.11, 5.12)
Looking at SEM results further information can be obtained, in fact from the comparison between the untreated and treated with water PVC, it can be observed the formation of holes and the reduction of white spots, previously assigned to CaCl$_2$. 
It’s interesting to notice that PVC treated with Agar gel doesn’t show the big holes previously seen, just a little porosity (fig 5.14). Moreover we can suppose Agar to be absorbed by the surface since the map of fig 5.15b shows the formation of phosphorous peak, typical of Agar, which doesn’t appear in the map relatives to the untreated specimen (fig 5.15a).
Chapter 5 Conservation treatments

Fig 5.14 SEM picture of PVC treated with Agar gel

Fig 5.15 map of constituents element for PVC before (a) and after treatment with Agar (b)
A situation similar to the first case, treatment with water, can be seen also with thiophene. Holes are formed on the treated surface (fig 5.16) but from the map of fig 5.17 no traces of Solfur, which is characteristic of 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene, can be observed. It can be supposed that the additive was not absorbed by the surface, at least not in significant quantity, and that the reduction in yellowness and formation of holes are caused by the presence of water.

FTIR spectra of treated and untreated specimens are shown for each case. (fig 5.18, 5.19, 5.20)
Chapter 5 Conservation treatments

Fig 5.18 FTIR spectra of PVC before (red) and after treatment with water (blue)

Fig 5.19 FTIR spectra of PVC before (red) and after treatment with Agar (blue)
Results from spectroscopic analyses constitute a further validation of what already supposed; Agar gel gave best results concerning the reduction of yellowness, moreover, the peak relatives to O-H bonds (3440 cm\(^{-1}\)) that is a typical sign of degradation, is more strongly reduced compared to the other cases. Its good cleaning properties, in addition to the lower aggressiveness on surface morphology, supported by SEM analyses, make Agar gel the best choice among the additives tested so far.
6. Conclusions

Specimens of PVC, PP, ABS, HDPE and LLDPE have been subjected to accelerated aging using an Arc Xenon lamp and a careful characterization have been carried out. From the obtained results, several considerations can be drawn.

As expected, PVC ABS and PP showed a stronger degradation with respect to the other plastics at equal aging time. This is confirmed by FTIR spectroscopy and colorimetric results.

The major consequences of UV light aging are found both in surface’s modification, morphology and colour (yellowing), and in mechanical properties, above all the tendency of plastics to become more brittle.

Examining the first consequence, it’s better to make a distinction between plastics. On PVC specimens, for example, the yellowing appeared in the form of small dark spots that, as aging proceed, increase in dimension and density. ABS surfaces showed an apparent homogeneous yellowing even if, with SEM analyses, the formation of cracks on the more degraded specimen could be seen. On PP specimens too, the change in color was accompanied by the formation of randomly oriented microcracks which the surface was completely covered and that were visible also with a Stereo microscope.

On the contrary, few variations were observed during HDPE and LLDPE degradation with FTIR spectroscopy as well as with microscopic and colorimetric analyses.

Thanks to scratch tests it was possible to investigate the variations in mechanical properties due to photo oxidation.

All the plastic specimens were tested setting scratch parameters in order to achieve the most damaging situation so that fractures or cracks formation could be visible. Scratch test results, supported by microscopic observation and SEM micrographs showed an increasing in brittleness for all the specimens with consequently formation of microcracks and debris production. Plotting the penetration depth (Pd) against the scratch length for each aging time further consideration could be done; in the cases of semicrystalline polymers (PP, HDPE, LLDPE), higher values of Pd were achieved with higher aging time while, considering the amorphous polymers (PVC and ABS) lower values of Pd were visible as aging time increased, concluding that the latter improved their hardness. Further analyses were carried out on PVC, setting scratch parameters so that a clear variation in mechanical properties with degradation could be seen. It resulted that, as expected, with higher load, and lower aging time, higher levels of depth were achieved, and that the trend followed by Pd as aging time increased were similar for each applied load. Moreover, observing the results, it could be noticed that, as aging time increased, also friction increased, concluding that surface characteristics modification, due to degradation, lead to a more difficult interaction with the tip probably because of a sticker surface was formed.
Chapter 6 Conclusions

With regards to the analyses concerning additivation with whiteners and cleaners on PVC, several conclusions can be drawn.

From spectroscopic, microscopic and colorimetric results it was observed that both 4,4′-Bis(2-benzoxazolyl)stilbene and 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene in solution with water and ethanol had good whitening properties but, since also water itself seemed to lower the yellowing, and the whiteners were in powder form, it was difficult to properly identify the additive effect and the water effect.

On the other hand, interesting results were achieved using Agar gel. When the thin layer of Agar was removed from the PVC surface a huge difference in colour was visible, confirmed by the following characterization analyses. Further analyses and investigation must be carried out on this innovative topic of study.

Two case studies were investigated, a desk lamps dated 1968 (“Telegono”) and another one dated 1965 (“KD 4335”). Characterization analyses were carried out on micro samples in order to define their constituent polymers. It was found out that “KD 4335” lamp and “Telegono” lamp shell and compartments were made of ABS while “Telegono” light globe was made of Polypropylene. Moreover analyses of samples taken at increasing depth from the surface were performed in different areas of the lamps in order to analyse degradation conditions. Comparing data obtained by the case studies with those achieved from the polymer’s specimens, consideration on the degree of degradation were drawn. Even if the two lamps belong to the same period of time, the “Telegono” parts made of ABS resulted more degraded with respect to “KD 4335” lamp, moreover, “Telegono” compartments could be compared with an aging time higher than 500h while “KD 4335” was comparable with a 100h aged ABS specimen.

For what concern PP light globe of “Telegono” lamp, a comparison with PP specimens were harder to be achieved; even if, from colorimetric results, an equal *b value was found for the lamp sample and the 250h aged specimen, further in-depth analyses must be carried out aimed at obtain a more realistic comparison.
7. References


[22] Global solar radiation available online: www.solaritaly.enea.it