Influence of wavelength specificity on the photodegradation effects of polymeric materials used in cultural heritage conservation

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Physico-chemical stability of various polymeric materials dedicated to the art market is being discussed as an analytic response under induced artificial ageing. On the basis of an extensive kinetic analysis, a series of correlation could be draw on regard the causes and mechanism of degradation affecting these class of materials by the use of Attenuated Total Reflectance (ATR) – FT-IR measurements and spectrophotometry. Experimental factors, such as the effect of wavelength specificity, on particular case studies, highlights practical aspects that further can be applied for an accurate characterization of the chemical processes involved in the photodegradation of this class of polymeric materials.

1. Introduction

In the last decades a wide variety of synthetic polymers were introduced within the art market that are now being currently used in a great number of applications [Asensio, 2009]. Coatings, adhesives, fixatives, varnishes, adhesives and consolidants, can be mentioned among the most frequently used products in conservation and restauration work. While the practical applications of these polymers depend on their composition and form (film, sheets, pressure-sensitive adhesives, heat-seal adhesives, foam, powders, etc.), their long term stability and ultimately their ageing characteristics are directly correlated with their chemical composition, which, as in the case of all modern art materials, comes as complex chemical formulations [Jablonski, 2003]. Molecular size distribution, degree of crystallinity, glass transition temperature (T_g), nature and proportions of certain additives or fillers added during manufacturing, are all factors that influence the physical and chemical properties of the final product [Learner, 2004]. Inevitably, all these properties change with time, and the material is said to undergo aging.

The generic term polymers covers a broad class of materials that consists of identical constitutional repeating units, monomers. Nature of the repeating units or nature of the defects within the structural sequence affects the overall properties of the material. The structure-properties relanshionship within a certain polymer is also dependent on the types of transitions that occur in such materials, in solid state a polymer being partially or totally amorphous and only exceptionally purely crystalline [Krevelen, 2009].

As shown in previous studies [Struik, 1977], aging follows a similar path in all glassy materials – whether polymeric, monomeric, organic or inorganic. Specific, at temperatures below their glass transition, amorphous solids are not in thermodynamic equilibrium, such materials being regarded as solidified supercooled liquids whose volume, enthalpy and entropy are greater than they would be in the equilibrium state [Struik, 1977]. Moreover, it was shown that for temperatures in the aging range, the time dependence of the small-strain mechanical properties of a glassy material is independent of the chemical structure of the material. In other words, physical ageing can be seen as a gradual continuation of the glass formation that sets around T_g, and affects all temperature-dependent properties that change dramatically at T_g. Nevertheless, we have to distinguish this type of phenomena from chemical ageing – photo-oxidation, thermal degradation, etc., that follows specific degradation pathways [Blaga, 1980; Maxwell, 2005]. According to the standard principles of photochemistry, in order to undergo a photochemical reaction a material must first of all absorb light energy [Feller, 1994]. Lambert-Beer's law specifies that the absorbance is directly proportional to the concentration of the absorbing substance and thickness of the material but does not depend on the intensity of the light source. Further, the Grotthus-Draper law states that only a fraction of the absorptions of photons at a specified wavelength leads to photolytic activity, the non-photolytically effective absorptions being dissipated as heat [Martin, 1994]. The type and extend of degradation will be thus wavelength dependent as it is largely determined by the absorption properties of the material (the fraction of

incident light at each wavelength that the material is capable of absorbing) and by the interaction of the absorbed light with the material [Searle, 1994]. It is the relation between the energies of the absorbed photons and the bond energies within the material that determine the type of bonds broken and thus the nature of chemical changes that occur. When exposed to UV radiation most polymeric materials will undergo photooxidative degradation which results in breaking of the polymer chains, free radicals formations and reduction of the molecular weight due to macromolecular chain bond scission or to an increase via crosslinking, all of the above phenomena causing deterioration of the mechanical properties [Yousif, 2013]. The probability and nature of a photochemical reaction following absorption of light is influenced by o series of factors, among: the surroundings of the excited molecule (whether it on a surface or interface; if it is near other molecules to which it can transfer its excitation energy or with which it can chemically react; if water molecules are present), and on the properties of the excited molecules themselves. For accelerated test procedures, due to material differences in absorption properties and bond energies, the spectral power distribution of the light source will be an important factor when trying to assess photodegradation mechanism. Activation spectra of common polymers have been mentioned in a number of studies [Searle, 1988; Andrady, 1992] along the effects observed over an extensive range of wavelengths [Bousquet, 1984; Gardette, 1986]. Lightfastness ranking [Whitmore, 1995], as well as surface versus bulk degradation in aromatic type polymers or antagonistic effects of spectral regions were also discussed [Searle, 1994]. Despite extensive research within the cultural heritage conservation field [Simileanu, 2011; Angheluta, 2011; Sadek, 2012], there are relatively few studies in the literature focused on these new class of conservation based materials and their ageing characteristics. In this paper we present a spectrometric study carried on several polymeric materials currently used in conservation and restauration work that were artificially aged under different UV conditions. General considerations on regard wavelength sensitivies and the relative effect of different spectral regions over the kinetic of reaction are further discussed.

2. Materials and methods

2.1 Samples

Various commercial materials currently used within the conservation and restauration practice were considered for testing (see Table 1). Samples were classified according to the chemical nature of the polymer: PEG 400, often used for waterlogged archaeological wood objects; Paraloid B72, an acrylic polymer widely used in conservation of cultural heritage; and three epoxy resins used especially as structural consolidants – Araldite SV 427, EPO 155, Balsite W. Selected materials were applied in thin layer on a wood substrate. Samples were artificially aged by exposure to different UV radiation sources (fluorescent lamps with emission peak at 350 nm and 253 nm) and periodically analyzed in order to assess potential changes. Influence of the characteristics of the radiation to which these materials were exposed is further discussed.

Table 1 – list and specifications of tested materials

Commercial name	Chemical formula / classification	Application	Observations regarding preparation
PEG 400* / Carbowax / Modopeg	$C_nH_nn+_2O_{n+1}$ Polyethylene glycol	wood consolidant	Long-term treatment involves progressively increasing the concentration of the consolidant.
Paraloid B72* / Acryloid B72	Thermoplastic acrylic resin comprised of methacrylate (70%) and ethyl acrylate (30%)	wood consolidant / adhesive	The concentrations used for the consolidation of wood can reach up to 20%. In concentrations higher than 20%, Paraloid B72 can be applied as adhesive. The most used solvent for consolidation is acetone (due to the high speed of evaporation).
Araldite SV 427*	Bicomponent thixotropic epoxy resin	wood putty / adhesive	Preparation mode: 100% Araldite SV 427 - epoxy resin, 100% HV 427 - hardner (weight ratio). The mixture has a brown paste appearence.
EPO 155*	Bicomponent epoxy resin	wood consolidant / adhesive	Preparation mode: 100% EPO 155 - epoxy resin, 50% HV K156 - hardner (weight ratio). The mixture is a colorless liquid. The product can also be injected.
Balsite W*	Bicomponent thixotropic epoxy resin	wood putty / adhesive	Preparation mode: 100% Balsite W - epoxy resin, 50% Balsite K - hardner (weight ratio). The mixture is a brownish pink color paste.

* These products are supplied by CTS Srl, http://www.ctseurope.com/

2.2 FTIR spectroscopy

FTIR spectra in attenuated total reflectance (ATR) mode of the film specimens were obtained using a PerkinElmer Spectrum Two FITR spectrometer equipped with a GladiATR accessory. Spectra were recorded in the min-infrared region 4,000 – 400 cm^{-1} at a resolution of 4 cm^{-1} by averaging 16 scans; no sampling preparation was required. A refinement of conventional FTIR spectroscopy, within ATR technique samples are directly pressed against a crystal window of relatively higher refractive index, the infrared beam interaction taking place at the level of this interface with the generation of an evanescent wave that further projects orthogonally into the sample. Molecular changes were evaluated by comparing absorption spectra obtained before and after artificially induced ageing, measurements providing an average film composition on its outer layer (depth in the 0.2-0.7 μm range).

2.3 Spectrophotometry

Reflectance curves were measured by means of a GretagMacbeth portable spectrophotometer. Color of the samples were also recorded within the CIELAB color system. Collected data, expressed as L*- darkness to lightness, a* - green to red color component, and b* - blue to yellow color component, were registered under the standard illuminant D65, using the 10° supplementary standard observer.

3. Results and discussion

Results are presented for each material separately, as a function of ageing. As we already mentioned, the relative effect of different spectral regions vary with the absorption characteristics of the investigated material (and its resistance to the absorbed radiation) as well as with the spectral power distribution of the light source used during exposure. Previous studies [Van Oosten, 1996] have cited changes in the oxidation state of high and low-density polyethylenes after 100 hours of exposure under UV light from a filtered xenon-arc source, while polyacrylates are generally considered stable when exposed to radiation above 300 nm [Feller, 1981] as well as epoxy resins when

properly formulated. However, enhanced yellowing by near-UV light may be observed when the ratio of hardener to resin is not within the guidelines for the particular formulation [Tennent, 1979].

3.1 FTIR analysis

As a general consideration, variations in band shapes (broadening) and relative intensities are observed between fresh and artificially aged samples. Specific, after the initial stages of exposure (above 50 hours) an increase within the characteristic absorption bands can be noticed - while the position maxima remains stable, the band relative intensities go higher. This behavior was observed for all tested materials under both light sources used during exposure, situation explained as a relaxation of the polymer chain segments. This effect is assumed to molecular rearrangements in regions of particularly high free volume produced by thermal fluctuations [Robertson, 1984].

In a series of publications begun in 1978, Robertson developed stochastic interpretation of the relaxation processes in glassy polymers near T_g. According to his studies [Utracki, 2010], the rate of the conformational changes that occur in localized groups of atoms in the chain backbone are coupled with the variable free-volume environment. This effect is linked with thermal fluctuations. At a temperature below its glass transition the chains have insufficient time to relax to their lowest-energy configuration. This nonequilibrium vitreous state is characterized by an excess of volume, and if held at a temperature under T_g it will attempt to achieve its thermodynamic equilibrium though a variety of localized molecular relaxation processes that manifest as changes in the physical and mechanical properties [Struik; 1980; Utracki, 2010].

As shown in Fig. 1 only small differences in FTIR spectra are appreciable for the accelerated aged samples of Balsite W and Araldite SV 427 in terms of photo-oxidation, in comparison with EPO 155 or Paraloid B72 (Fig. 2) that shows signs of specific degradation pathways. The decrease or disappearance of certain bands can be ascribed to rapid oxidation processes, while the increase in intensity of others suggests the accumulation of molecular modifications within the aged samples [Nevin, 2009].
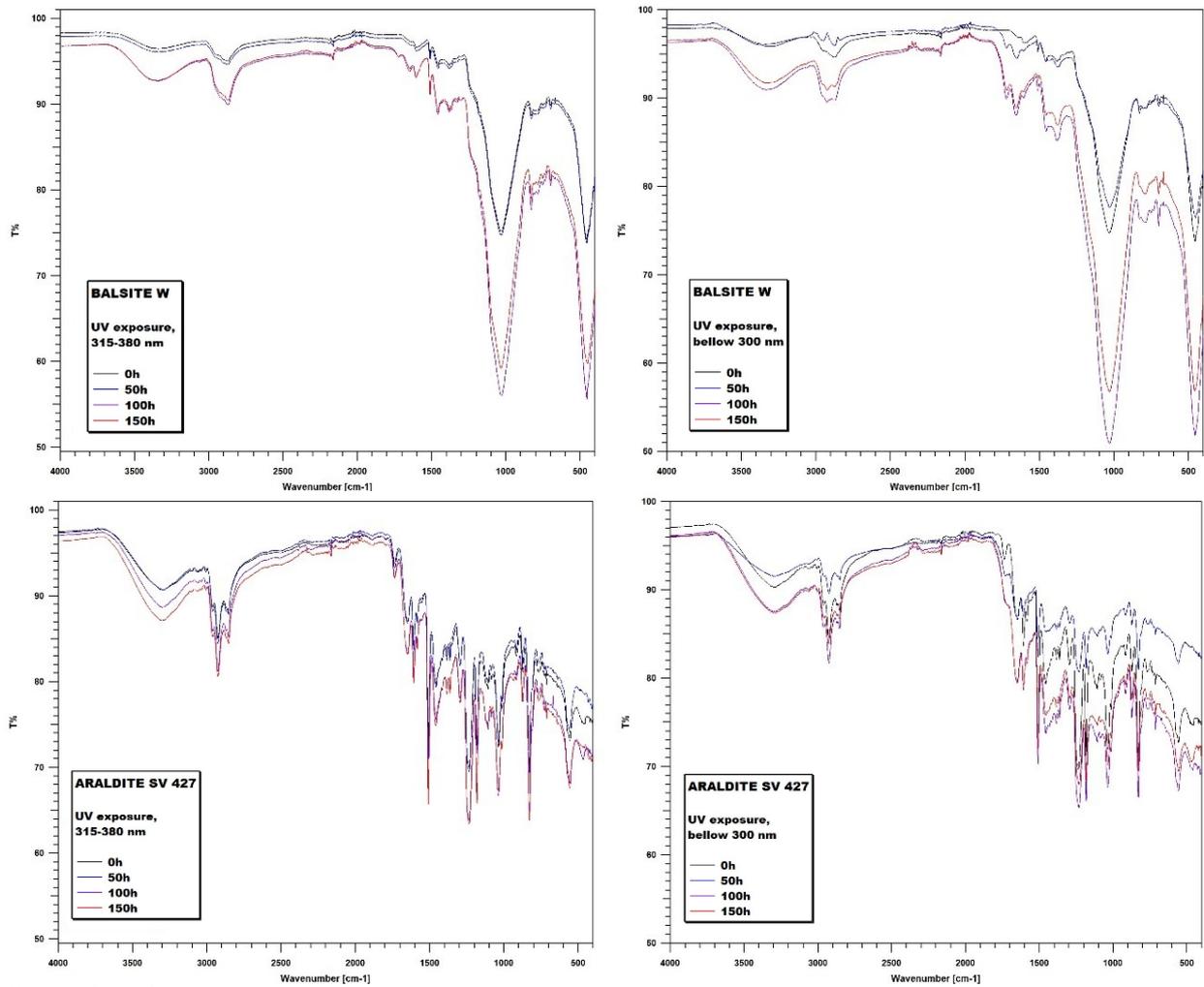
FIG. 1. ATR-FTIR spectra of fresh and artificialy aged materials within the epoxy resin family; each plot is a spectral overlay of samples that were gradually exposed under flourescent lamp radiation (spectra are given for both light sources used during exposure); note that the absorption position maxima remains stable while the band relative intensities present changes; the shortest bands coresponds to the fresh, unaged samples, while the tallest coresponds to high exposure hours.
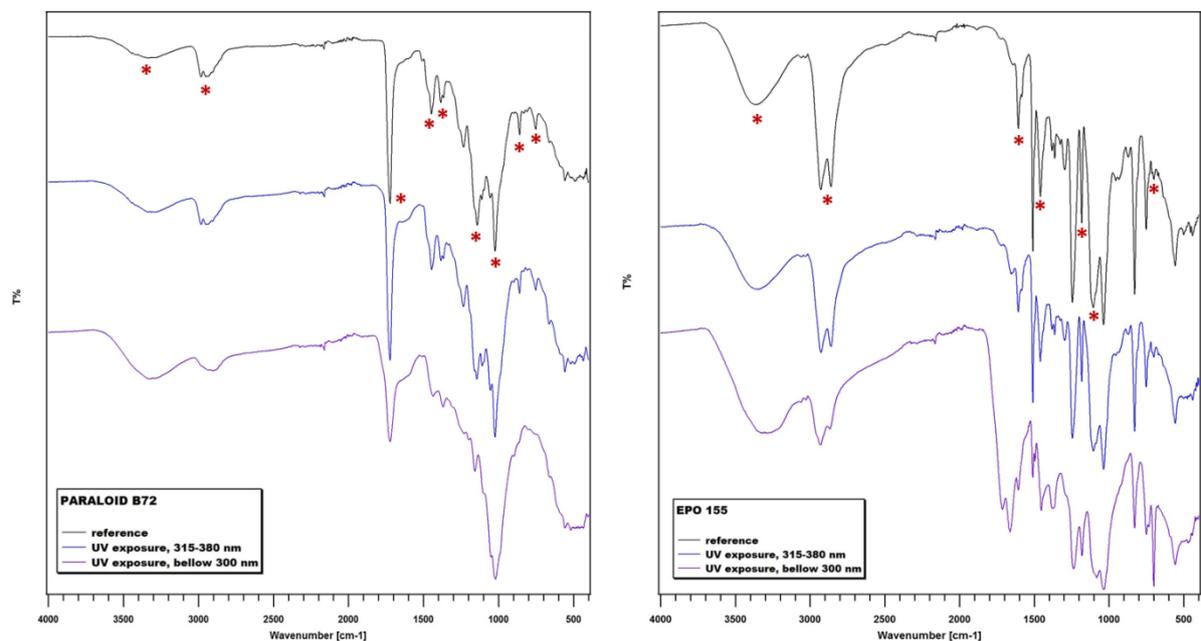

FIG. 2. IR spectra of films of Paraloid B72 and EPO 155 registered for the 150 hours exposed samples; spectra have been plotted with an offset for better comparation; peaks with changes are marked.

Specific, for the Paraloid B72 aged samples oxidation can be ascribed to changes observed for bands at 2982, 2950, 2870 cm^{-1} (due to asymmetric and symmetric stretching of the -CH$_3$ groups), 1723 cm^{-1} (C=O stretching vibration), 1646 and 1384 cm^{-1} (asymmetric and symmetric in-plane bending C-H(-CH2-)), 1022 cm^{-1} (–CH$_3$ rocking and -CH$_2$- wagging bending modes), 858 and 753 cm^{-1} (-CH$_2$- rocking). As can be clearly seen from the registered FTIR spectra, these band variations are more intense in terms of molecular changes and rate of degradation under shorter wavelengths of exposure. The same tendency is observed for EPO 155 where significant molecular changes are seen for samples exposed to radiation bellow 300 nm. In this case for the unexposed (reference) material the bands of interest are those at 1037 cm^{-1} (due to the C-O-C stretching of ethers), 1245 cm^{-1} (C-O stretching of the aryl-ether groups), 1510 cm^{-1} (C=C stretching of the benzene ring) and 3400 cm^{-1} (hydrogen bonded O-H stretching). Intense broadening within the fingerprint region (1700-1000 cm^{-1}) with loss of spectral features suggests formation of oxidation products; under short UV exposure wavelengths the intensities of these bands decreased while new bands appeared around 1660 cm^{-1} and 1715 cm^{-1} that can be assigned to the C=O stretching modes of amide and ketones [Rezig, 2006]. Similar, small but significant changes in the IR spectra of PEG 400 were detected in the aged materials, the most prominent feature being an intense band with a shoulder around 1717 cm^{-1} that suggests the presence of more types of carbonyl compounds.

Further, for a better correlation of the results a relation between measured FTIR signatures and surface optical changes during exposure was questioned.

3.2 Spectrophotometric data

All consolidants have shown the same tendency, of diminished reflectance, as the exposure time increased. Fig. 3 shows the reflectance curves acquired for the PEG 400 aged samples, under the two exposure wavelengths regimes, 315-380 nm UV emission region and below 300 nm, respectively. Analyzing the obtained data we can assume that a greater influence comes from the exposure regime than from the exposure time. Previous studies [Rezig, 2006] have asserted that the thickness loss of an unpigmented polymer coating exposed to UV is directly proportional to the loss of the CH groups in the film, based on the assumption that chemical degradation (represented by the CH loss) can be attributed to a homogeneous and uniform ablation process. However, polymeric surfaces exposed to UV radiation degrade non-homogeneously, situation that could explain our experimental spectrophotometric data. UV exposed samples undergo a general and constant reflectance decrease on the entire visible region, situation assumed at optical level as a gradual loss of gloss. Specific features, as a decrease within the blue region of the spectrum more evident for the PEG, Paraloid and Balsite samples correlates with a yellowing effect, while changes within the red area of the spectrum (600-750 nm) in the case of EPO and Araldite exposed samples (see Fig. 4) corresponds to a darkening and browning effect, situations confirmed by the registered chromatic coordinates.
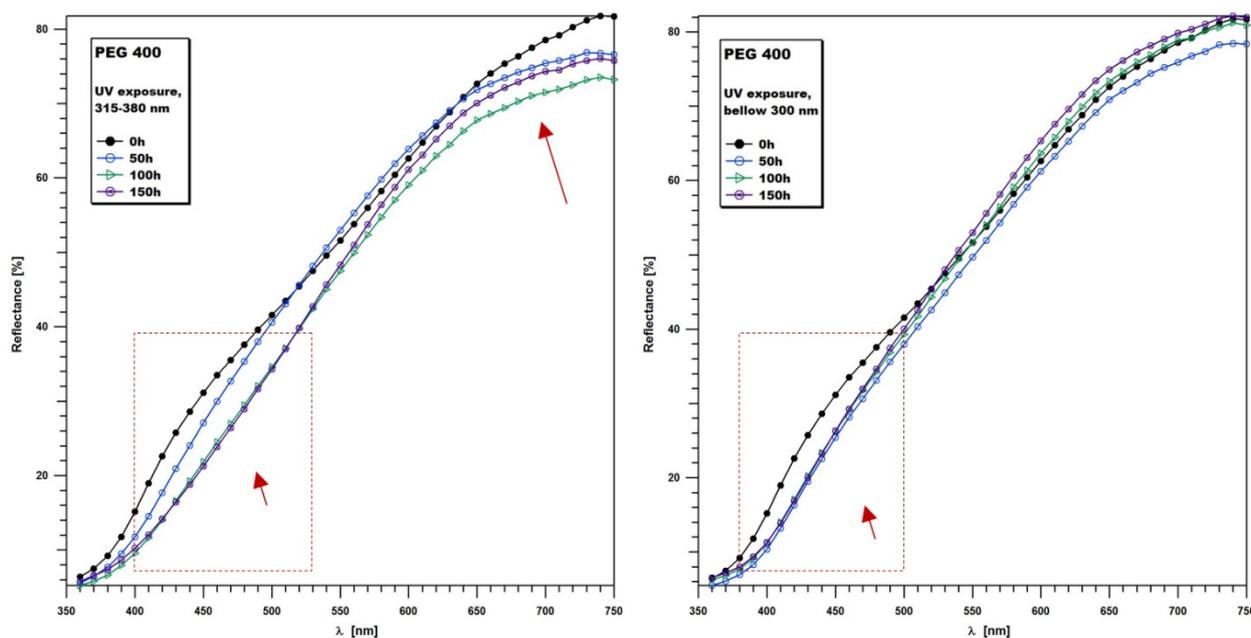

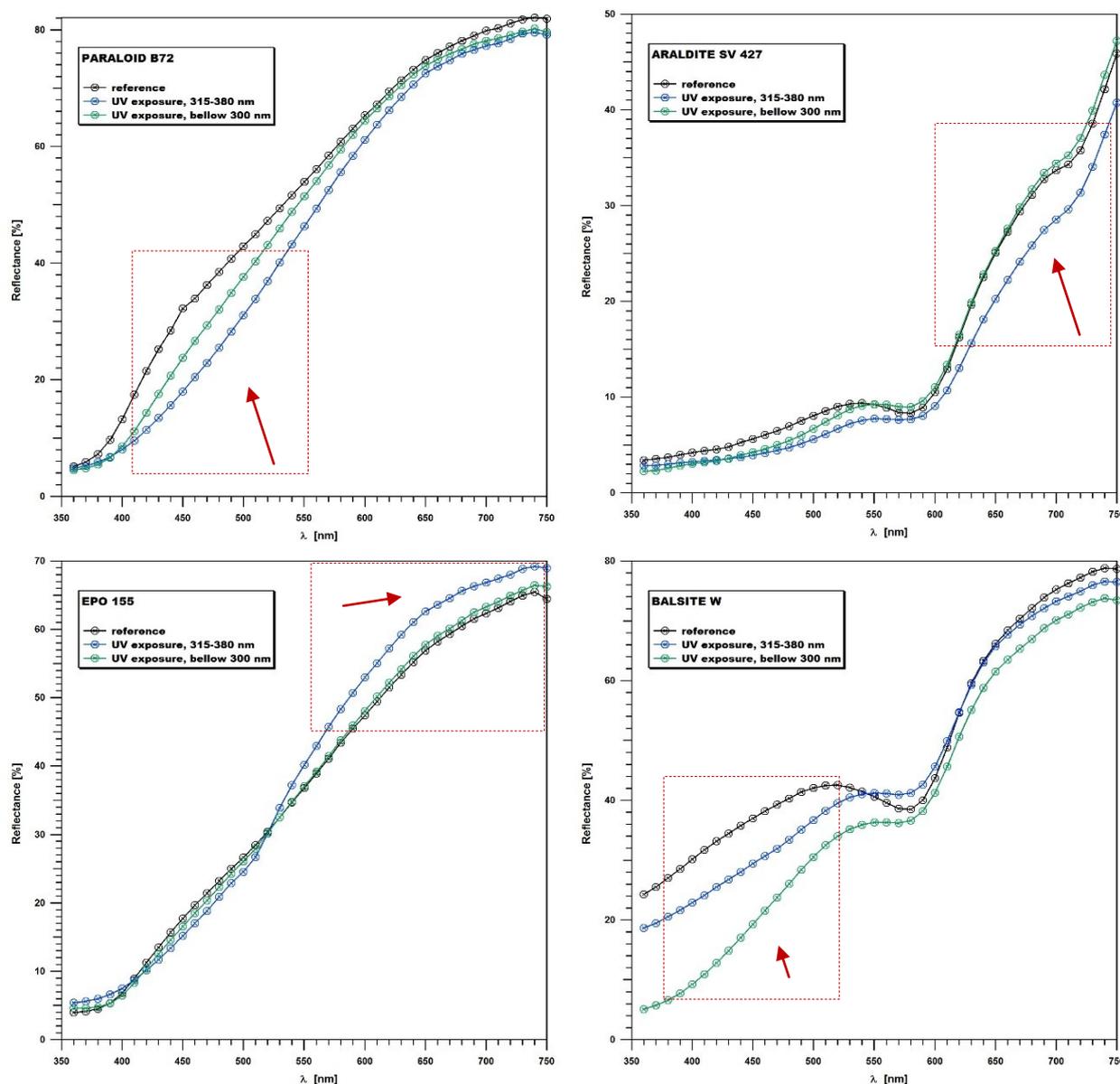*FIG. 3. Reflectance curves recorded for PEG 400 samples at progressive stages of the exposure tests.*

Fig. 4. Reflectance curves recorded for selected materials; areas of analytical interest are marked (reflectance curves of the UV exposed samples are given for the 150 hours threshold).

The decrease of the reflectance curves can also be linked to the fact that visual colors are affected by the treatment the samples were subjected to [Kerekes, 2008]. A similar behavior has been observed for filter paper made out of wood fibers, without additives. Plazonic and co-workers [Plazonic, 2009] have observed that near UV and visible electromagnetic radiation lead to a significant decrease of the reflectance spectra, especially in the blue region, whilst chemically treated samples appeared to be more stable. A much earlier study provides a landmark on the irradiation wavelength specificity on the effects induced in accelerated aged materials. Launer [Launer, 1965] observed that wool samples were mostly affected by the 365 nm wavelength, which caused increased absorption and bleaching. Feller [Feller, 1977] offered an explanation for the declining rate of the UV-induced

effects observed putting it on the depletion of a limited number of particularly photosensitive sites.

With several ageing mechanisms of different velocity that superimpose, the relation between materials response to wavelength specificity proves complex. Additives and minor components present within the chemical formulation of these products affects the overall properties of the materials, their physico-chemical stability, ageing characteristics and nevertheless their light sensitivity. All functional groups present within the material – compounds in the main polymer, impurities, stabilizers, etc.– have specific absorption mechanism that not necessarily overlap. Moreover, a number of factors can be made responsible for causing photodegradation [Schnabel, 1981], such as (1) internal impurities which may contain chromophoric groups introduced during polymerization processing and storage (hydroperoxide, carbonyl, catalyst

residue, unsaturated bonds) and (2) external impurities, which may include chromophoric groups as well - additives, traces of solvents, traces of metals and metal oxides, compounds from a polluted urban atmosphere. It is often due to the presence of these chromophores that polymers absorb near-ultraviolet (UV) or visible light, while the presence of various additives or impurities increase the light-sensitivity of a polymer [Schaeffer, 2001].

Another important parameter when talking about consolidants is the degree of impregnation. The rate of penetration and distribution of the consolidants applied depend on their relative molecular weight and concentration of its solution [Kucerova, 2012], in other words on its viscosity. This topic will not be discussed here but rather we will try to evaluate the extent of surface versus bulk degradation. Previous studies focused on wavelength dependence surface and bulk reactions have shown that in most type of aromatic type polymers, degradation promoted under short wavelength UV radiation will be largely confined to the surface layers [Searle, 1994], in contrast to long UV radiation that penetrates deeper into the material as these wavelengths are being weakly absorbed. In poly(methylmethacrylate) exposed under 265 nm radiation it was observed that the loss of molecular weight was not particularly sensitive to film thickness, but rather an effect of the increased absorption [Henning, 1981]. These dependences will further affect the effectiveness of UV stabilizers introduced within the material during synthesis, and explain the color variations registered upon exposure [Munro, 1985].

By correlating the spectrophotometric response with the FTIR data we could assume that with exposure the surface roughness increases. This topographic changes will scatter IR radiation and if sufficiently severe this scattering effect could reduce the amount of IR radiation reaching the detector. The transmittance, ratio between detected and incident intensity should decrease, situation that apparently is not confirmed. As the intensity of an IR band is directly proportional to its absorption coefficient, normalization against the bands' initial values should allow a direct comparison of the degree of different degradation processes. Nevertheless, we have to remember that degradation of macromolecules in polymeric materials infer all process which lead to a decline of polymer properties, either physical or chemical. All these degradation mechanism, some antagonistic, along particular wavelengths sensitivities that promotes specific surface chemical changes, can hide a liner response in terms of FTIR intensities.

4. Conclusions

The importance of having a detailed knowledge of the materials response, behavior and ageing characteristics is crucial in trying to prevent and ultimately minimize any chemical and physical changes that may induce damage to the artwork. Due to the molecular nature of the materials that is directly linked with their absorption characteristics, the differences in wavelength sensitivities can be correlated with specific degradation pathways. Recorded data analyzed in this work showed that the ageing mechanism of polymeric materials exposed under UV conditions follows a complex kinetic of reactions. Degradation mechanisms will frequently be promoted via additives present within the formulation and not necessarily via the main functional groups within the polymer. By correlating FTIR spectra with spectrophotometric data we were able to highlight the importance of the spectral power distribution when used to reliably evaluate the degradation effects induced under short versus long UV wavelengths exposure. During the physical ageing of a polymer the chemical structure remains unchanged, but due to the slow structural relaxation of the glass the local packing of the chains is altered. This has important practical consequences as it determines the behavior and performance of the material. Unlike physical ageing, chemical ageing is nonreversible and leads to a degradation of polymer properties - discoloration, yellowing, brittleness.

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