CHARACTERIZATION OF CHANGES IN THE CHEMICAL COMPOSITION OF AGED ACRYLIC RESINS USED IN CONTEMPORARY ARTWORKS

María Teresa Doménech-Carbó, Giovanna Bitossi, Dolores Julia Yusá-Marco and Laura Osete-Cortina
Instituto Universitario de Restauración del Patrimonio de la Universidad Politécnica de Valencia
Laboratorio de Análisis Físico-Químico y Control Medioambiental de Obras de Arte

CORRESPONDING AUTHOR: María Teresa Doménech Carbó, tdomenec@crbr.upv.es

ABSTRACT: *The present work focuses on the study of changes in composition taking place during the ageing of acrylic resins currently used in contemporary art by combining the spectroscopic techniques UV-visible spectrophotometry and FTIR spectroscopy and the chromatographic technique of pyrolysis-gas chromatography-mass spectrometry. The proposed instrumental techniques have been applied to a series of acrylic test specimens. Preparation procedures have been developed in order to obtain relevant information on the chemical changes produced during an accelerated ageing processes based on exposure to both UV light and SO_2 pollutant.*

KEYWORDS: Py-GC-MS, FTIR spectroscopy, UV-VIS-Spectrophotometry, acrylic resins, artwork

INTRODUCTION

Analysis of contemporary works of art is faced with a formidable challenge due to the continuous incorporation of new synthetic polymers in paint, varnish and priming formulations. On the other hand, environmental conditions such as light, fluctuating relative humidity and temperature, atmospheric pollution as well as human activities usually cause the deterioration of these materials. This problem has attracted the attention of an increasing number of conservators, curators and scientists involved in the cur e of contemporary art objects. In particular, acrylic resins have been studied given their wide use in conservation studio practice. Thus, a number of works have been reported in literature, focusing on the characterisation of synthetic paints (Sonoda and Rioux, 1990; Stringari and Pratt 1991; Learner, 1995; Learner, 1996; Sonoda, 1998; Derrick, 1999; Learner, 2001; Edwards and Chalmers, 2005; Osete-Cortina and Doménech-Carbó, 2006; Doménech-Carbó et al., 2006), influence of pigments (Spathis et al., 2002) and the study of the effects of natural and accelerated photoageing (Feller et al., 1985; Whitmore and Colaluca, 1995, López-Ballester et al., 1999; Whitmore et al., 2002; Ragauskienè et al., 2004). On the other hand, this type of synthetic resin has been slowly extending the scope of applications due to its proved stability in comparison to other synthetic resins and thus, a growing use of acrylic resins as binders or to coat objects of art that are exposed to the outdoors, or a consolidant of monuments, has been reported in recent years (Spathis et al., 2002). In contrast, very few papers focusing on the characterisation of changes due to the influence of atmospheric pollutants have been reported in the literature.

The present work centres on the study of changes in composition taking place during the ageing of acrylic resins currently used in contemporary art by combining spectroscopic techniques, UV-visible spectrophotometry and FTIR spectroscopy, as well as the chromato-graphic technique of pyrolysis-gas chromatography-mass spectrometry. The results summarised herein have been obtained in the first series of experiences programmed in the Spanish "I+D+I MEC" project CTQ2005-09339-CO3-01 devoted to the development of new analytical methods for the characterisation of synthetic resins used in contemporary works of art, the identification of microbiological alterations and the control of biocide treatments. For this purpose, the proposed instrumental techniques have been applied to a series of acrylic test specimens. Preparation procedures have been developed in order to obtain relevant information on the chemical changes produced during accelerated ageing processes based on exposure to both UV light and SO_2 pollutant.

EXPERIMENTAL

Instrumentation and procedures

Experiments were carried out with an integrated system composed of a CDS Pyroprobe 1000 heated filament pyrolyser (Analytical Inc., New York, USA), and a Gas chromatograph Agilent 6890N (Agilent Technologies, Palo Alto, Ca., USA) coupled to an Agilent 5973N mass spectrometer (Agilent Technologies) and equipped with a pyrolysis injection system. A capillary column HP-5MS (5% phenyl-95% methyl-polysiloxane, 30 m x 0.25 mm I.D., 0.25 μm film thickness, Agilent Technologies) was used in order to provide the adequate separation of components.

Pyrolysis was performed at 700ºC for 10 s. using a precalibrated Pt coil type pyrolyser (CDS pyroprobe). The pyrolyser interface and the inlet were set at 250ºC. The samples were injected in the split mode (split ratio 1:80). The chromatographic conditions were as follows: initial temperature of 50ºC increased at 5ºC.min^{-1} up to 100ºC increased at 15ºC.min^{-1} up to 295 held for 2 min. Helium gas flow was set at 1.2 ml.min^{-1}.

Acrylic resin	Un-aged resin	Photoageing	SO$_2$ pollutant ageing
Main absorption bands			
BMA type			
Elvacite 2044	Continuous absorption below 300 nm with two overlapped sharp bands with maximum at 285 nm and 340 nm	Prominent band at 285 nm Small and broad band at 340 nm	Sharp bands at 285 nm and 340 nm
Elvacite 2046	Continuous absorption below 300 nm with an overlapped sharp band with maximum at 285 nm	Prominent band at 285 nm Small and broad band at 340 nm	Prominent band at 285 nm Slight increase of the background absorption in all the Visible spectrum
Paraloid B-67	Continuous absorption below 285 nm	Continuous absorption below 285 nm	Continuous absorption below 285 nm
Plexisol P 550	Conti nuous absorption below 300 nm	Prominent band at 285 nm	Continuous absorption below 300 nm with an overlapped sharp band with maximum at 285
BMA-OMA type			
Plexigum PQ 611	Continuous absorption below 285 nm Slight background absorption in all the Visible spectrum	Prominent band at 285 nm	Prominent band at 285 nm
BA-MMA type			
Plextol D-498	Continuous absorption below 285 nm	Prominent band at 285 nm	Prominent band at 285 nm
Primal AC-35	Continuous absorption below 300 nm with an overlapped sharp band with maximum at 285 nm Small and broad band at 330 nm	Broadening of the band at 285 nm	Continuous absorption below 300 nm with an overlapped sharp band with maximum at 285 nm
BA-BM-MMA type			
Primal E-330-S	Continuous absorption below 300 nm Short and broad band at 330 nm	Prominent band at 285 nm	Prominent band at 285 nm Significant increase of the background absorption in all the Visible spectrum
EA-MMA type			
Paraloid B-82	Continuous absorption below 285 nm Slight background absorption in all the Visible spectrum	Prominent band at 285 nm	Prominent band at 285 nm
Plextol B-500	Continuous absorption below 285 nm	Prominent band at 285 nm	Prominent band at 285 nm Significant increase of the background absorption in all the Visible spectrum
Primal AC-33	Continuous absorption below 300 nm Slight background absorption in all the Visible spectrum	Prominent band at 285 nm	Continuous absorption below 285 nm Significant increase of the background absorption in all the Visible spectrum
Primal B-60	Continuous absorption below 300 nm with an overlapped sharp band with maximum at 285nm Short and broad band at 330 nm	Broadening of the band at 285 nm	Continuous absorption below 300 nm with an overlapped sharp band with maximum at 285nm
MA-EMA type			
Paraloid B-72	Continuous absorption below 285 nm Slight background absorption in all the Visible spectrum	Prominent band at 285 nm Shoulder at 340 nm and weak peak at 390 nm	Prominent band at 285 nm Shoulder at 340 nm and weak peak at 390 nm

Table 1

The inlet pressure of the carrier gas was 67.5 kPa. The electronic pressure control was set to the constant flow mode with vacuum compensation.

Ions were generated by electron ionisation (70eV) in the ionisation chamber of the mass spectrometer. The mass spectrometer was scanned from m/z 20 to m/z 800, with a cycle time of one second. An Agilent Chemstation software G1701CA MSD was used for GC-MS control and mass spectra evaluation. Tuning of the Mass Spectrometer was checked using perfluoro-tributylamine (PFTBA). EI mass spectra were acquired in the total ion monitoring mode. The temperatures of the interface and the source were 280ºC and 150ºC, respectively. The Wiley Library of Mass Spectra was used for identifying compounds.

Samples were placed into a micro quartz pyrolysis tube and then two small portions of quartz wool were placed on both sides of the quartz tube in order to avoid undesirable displacements of the sample. After this, 2 μL of HMDS derivatisation reagent were added. Afterwards, the sample was placed in the pyrolysis coil and introduced into the pyrolysis interface, which was kept at 250ºC.

IR absorption spectra were performed in attenuated total reflectance mode (ATR) with a Vertex 70 Fourier transform infrared spectrometer with a FR-DGTS (fast recovery deuterated triglycine sulfate) temperature-stabilized coated detector. Number of co-added scans: 32; resolution: 4 cm-1.

Spectra in the UV and visible region were measured using quartz microcells in a Hitachi U2010 recording spectrophotometer.

Acrylic resin	Main IR absorption bands		
	Photoageing 12 h	Photoageing 72 h	SO$_2$ pollutant ageing
BMA type			
Elvacite 2044	Intensity decrease at 1472-1027 cm^{-1}	Band at 1640 cm^{-1} associate to the stretching vibrations of C=C bonds	No remarkable changes were observed
Elvacite 2046	No remarkable changes were observed	Band at 1640 cm^{-1} associate to the stretching vibrations of C=C bonds	Band at 1640 cm^{-1} associate to the stretching vibrations of C=C bonds.
Paraloid B-67	Intensity increase of band at 1724 cm^{-1} (ν_{CO}) 1392-	Band at 1780 cm^{-1} ($\nu_{lactones}$)	No remarkable changes were observed
Plexisol P 550	No remarkable changes were observed	No remarkable changes were observed	No remarkable changes were observed
BMA-OMA type			
Plexigum PQ 611	No remarkable changes were observed	No remarkable changes were observed	No remarkable changes were observed
BA-MMA type			
Plextol D-498	No remarkable changes were observed	No remarkable changes were observed	No remarkable changes were observed
Primal AC-35	Decreasing of band at 1505 cm^{-1} associated to bending vibration of (δ_{NH})	No remarkable changes were observed Band at 1640 cm^{-1} associated to the stretching vibrations of C=C bonds	No remarkable changes were observed
BA-BM-MMA type			
Primal E-330-S	No remarkable changes were observed	No remarkable changes were observed	No remarkable changes were observed
EA-MMA type			
Paraloid B-82	Intensity increase of band in the finger print region	Intensity increase of band in the finger print region	No remarkable changes were observed
Plextol B-500	No remarkable changes were observed	Band at 1780 cm^{-1} associate to the stretching vibrations of γ-lactones	Band at 1780 cm^{-1} associate to the stretching vibrations of γ-lactones
Primal AC-33	No remarkable changes were observed	No remarkable changes were observed	No remarkable changes were observed
Primal B-60	Decrease of band at 2885 cm^{-1} associated to (ν_{CH2}) and band at 2736 cm^{-1} ascribed to the stretching vibrations of aldehyde group. Decrease of band at 1505 and 1112 cm^{-1} associated to bending vibration of (δ_{NH}) and (ν_{CN}) Band at 1640 cm^{-1} associated to the stretching vibrations of C=C bonds and band at 3010 cm^{-1} associate to the stretching vibrations of H-C=	Intensity increase band at 1640 cm^{-1} associated to the stretching vibrations of C=C bonds and band at 3010 cm^{-1} associate to the stretching vibrations of H-C=	Band at 1640 cm^{-1} associate to the stretching vibrations of C=C bonds. Band at 3010 cm^{-1} associate to the stretching vibrations of H-C= bonds.
MA-EMA type			
Paraloid B-72	Intensity increase of band at 1724 cm^{-1} (ν_{CO}) 1392-	Intensity increase of band at 1724 cm^{-1} (ν_{CO}) 1392-	No remarkable changes were observed

Table 2

R_{ds-t}		
Unaged resin	Photoaged resin	SO$_2$ pollutant aged resin
0.35	0.34	0.54
0.57	0.44	0.40
0.66	0.34	0.82
0.53± 0.16	0.37± 0.06	0.59 ±0.21

Table 3

Artist's materials

The following products, supplied by G.C. Agar-Agar (Vigo, Spain), were used to prepare specimens owing to their wide use for preparing varnishes in conservation studio practices:
Acrylic resins Paraloid B72 (copolymer of ethyl methacrylate-methyl acrylate 70/30), Paraloid B67 (isobtyl methacrylate) and Paraloid B82 (ethyl acrylate-methyl methacrylate) and acrylic dispersions Plextol B500, Primal AC33 (ethyl acrylate-methyl methacrylate) and Plextol D498 (n-butyl acrylate-methyl methacrylate) manufactured by Rhöm & Haas. Plexisol P 550 (n-butyl methacrylate) (Rhöm). Elvacite 2046 (n-butyl methacrylate-isobutyl methacrylate) (Dupont). Plexigum PQ 611 (iso-butyl methacrylate-octyl methacrylate) (supplied by Kremer).

Preparation of acrylic specimens

A series of test specimens were prepared by applying the resin directly onto glass slides. In the instances where the resin was supplied as solid product solutions ranging between 1-5% in acetone, ethanol or xylene were prepared. The freshly prepared model specimens were spread as a thin layer on glass slides with the help of a thin pencil so that thin films with a thickness of less than 10 μm were obtained. Then, the specimens were naturally set in the dark at room temperature and relative humidity (approximate mean 20ºC 40%) for 1 month prior to testing.

Ageing treatments

UV light ageing

In the light exposure test, specimens were irradiated in a Dycometal chamber model QUV-Basic. The temperature was maintained at a constant value of 45ºC. A fluorescent UV lamp UVB model QUVB-313EL, with a maximum emission radiation at 295 nm, has been used. Independent measurements were taken after 12h, 24h, 36h, 60h and 48h exposure, respectively.

SO$_2$ pollutant ageing

Ageing was performed in a SO$_2$ chamber Dycometal model VCK-300 prepared for test DIN - 50.018 (the Kesternich test). Specimens were maintained in a polluted atmosphere for 15 days. Temperature and relative humidity were maintained at constant values of 40ºC±1ºC and 100%. The concentration of SO$_2$ during the experiment was maintained at a constant value of 2 l/g.

RESULTS AND DISCUSSION

UV-Visible Spectrophotometry

Unaged resins: The acrylic resins, in general, exhibited an absorption spectrum after 1 month of natural setting in the dark, characterised by a strong absorption below 300 nm with the presence of a prominent absorption band and with a maximum at 280 nm, frequently accompanied by a band at 240 nm and a less frequent weak band at 215 nm. A small band is also present in the Primal AC35, E330

and B60 resins, which exhibit a maximum at 340 nm. A band at 280 nm has been associated with acrylic dispersions to the presence of non-ionic surfactants containing the benzene ring (Whitmore and Colaluca, 1995).

Photoageing: Two different behaviours have been observed in the series of specimens, as summarised in Table 1. A band, with an absorption maximum at 340 nm, appears in the two Elvacite resins. The shoulder at this wavelength was found in the Primal AC 35 and Paraloid B72 resins. These bands could be associated with conjugated chromophores related to the chemical crosslinking responsible for the formation of the polymer film. The presence of specific catalysts in these resins can induce reactions with several polymer chains, resulting in solubility loss and discoloration (Hamm et al., 1993). Another possibility is that this band is produced by the incorporation of polar groups in the polymer chains during oxidative degradation taking place during photoageing. In contrast, the band appearing at 340 nm and the small and sharp peak at 380 nm in the unaged Primal AC35, E330 and B60 resins, is not found in the aged specimens. A slight increase of absorption across a broad wavelength region is observed in the Paraloid resins. These results are consistent with photobleaching studies previously reported on acrylic resins (Whitmore and Colaluca, 1995).

SO$_2$ pollutant ageing: Specimens subjected to this type of ageing exhibited similar spectra to those exposed to photoageing. Additionally, the acrylic dispersions Plextol and Primal exhibited a significant growth of the background signal. This result is consistent with the observation that the exposure of these acrylic films to atmospheric pollutants generally caused discoloration due to bleach. In a similar way, a slight increase of the background signal was observed in Elvacite resins. The increase of absorption across a broad wavelength region suggests a similarity to the chromophores which are produced in vinyl polymers, such as polyvinyl alcohol, as consequence of the formation of carbon chains containing conjugated double bonds (Whitmore and Colaluca, 1995).

FTIR Spectroscopy

Unaged resins: Acrylic resins, in general, exhibited characteristic bands at 2849, 2885, 2952 and 2980 cm^1 associated with stretching vibrational modes of the hydrocarbon skeleton. A prominent peak at 1726 ascribed to the stretching vibration of the carbonyl from ester groups also appears. In the finger print region, bands at 1453 and 1381 cm^{-1} have been ascribed to the asymmetric and symmetric in-plane bending vibrations (δ C-H) of the polymer skeleton, and sharp bands at 1240, 1161 and 1027 cm^{-1} have been ascribed to the asymmetric and symmetric stretching vibrations (ν C-O) of ester groups (Doménech-Carbó et al., 2006). It is interesting to note that Primal B60 exhibited a sharp band at 2885 cm^{-1} together with bands at 2736 and 2688 cm^{-1} associated with the aldehyde groups, as well as the two series of periodic bands at 1505, 1540, 1558 and 1577 cm^{-1} decreasing intensity and 1634, 1647, 1652 and 1687 cm^{-1} associated with the aromatic ring.

Photoageing: An increase in the intensity of the band appearing at 1640 cm^{-1}, ascribed to the double bonds, was observed in the Elvacite resins. According to what was found in the UV-Vis spectra, this band is associated with the formation of conjugated chromophores related to the chemical crosslinking responsible for the formation of the polymer film. The Primal B60 resin showed a significant decrease of the prominent band at 2885 cm^{-1} associated with stretching vibrations of -CH$_2$, a band at 2736 cm^{-1} ascribed to the stretching vibrations of the aldehyde group. Furthermore, a remarkable decrease of the band was noted at 1505 and 1112 cm^{-1} associated with the bending vibration of the NH- groups and the stretching vibrations of the CN group present in the ammoniated pH buffer that is usually added to these dispersions to increase thickener efficiency. In parallel, a weak band at 1640 cm^{-1} associated with the stretching vibrations of double bonds and a band at 3010 cm^{-1} associate with the stretching

vibrations of the H-C= bonds appeared in the IR absorption spectra of photoaged specimens, suggesting the formation of conjugated double bond chromophores related to the chemical crosslinking responsible for the formation of the polymer film and its discoloration. Primal AC35 exhibited decreasing of a band at 1505 cm^{-1} as well as the appearance of a band at 1640 cm^{-1}.

SO_2 pollutant ageing: IR absorption spectra of unaged and aged acrylic resins were similar, except for that corresponding to Primal B60 in which the aforementioned bands corresponding to additives were completely lots. The formation of conjugated double bond products was also observed in this specimen.

Py-GC-MS

The chromatogram of acrylic resins is characterised by the appearance of different groups of peaks corresponding to the monomeric, dimer, trimer and sesquimer fractions of the polymer (Osete-Cortina and Doménech-Carbó, 2006). Plextol B500 was selected from the set of resins studied in order to obtain complementary information and to find possible changes occurring during the two accelerated ageings tested on the resins other than those reported in the spectroscopic methods. Pyrograms from three replicates of specimens of this resin were obtained before and after SO_2 pollutant and photoageing. The pyrograms obtained at 700°C from Plextol B500, an ethyl acrylate-methyl methacrylate type resin (EA-MMA), include peaks appearing in the 5-16 min t_R range, corresponding to the different monomers present in the polymer, namely, ethyl acrylate (EA), methyl methacrylate (MMA). Interestingly, methacrylic acid occurs entirely as the trimethylsilyl derivative (TMSMA). This fact evidences the efficiency of the proposed reagent for derivatisation the studied polymer during the pyrolysis process.

In addition to the monomeric fraction, two families of compounds were identified in the pyrograms of the resins analysed, the first with peaks appearing between 15-18 min., which consists of sesquimers and dimmers, and a second group in the range between 20-25 min. associated with trimers. The oligomeric fragments identified have different chemical compositions depending on the sequence of monomeric units. Two sequences are particularly abundant in Plexto B500, EA-EA and EA-MMA, suggesting that they are present to a noticeable extent in the polymeric structure, although the sequence MMA-MMA has not been detected in the pyrogram, either indicating that this arrangement is not present in the polymer or its low stability contributes to the complete fragmentation during pyrolysis in the monomeric unit. On the other hand, an examination of the trimer fraction of this acrylic polymer revealed the prevalence of the sequence EA-EA-EA over the rest of the permutations of the EA and MMA units. The other arrangements detected were 2EA-MMA (EA-EA-MMA and EA-MMA-EA) and 2MMA-EA with the lowest intensity (Osete-Cortina and Doménech-Carbó, 2006).

Useful information concerning changes occurring after ageing can be obtained from the R_{ds-t} parameter defined as the quotient of the overall peak area, A, corresponding to the fractions of sesquimers/dimers and trimers.

$$R_{ds-t} = \frac{\sum_{ds=1}^{n} A_{ds}}{\sum_{t=1}^{m} A_t}$$

Where A_{ds} is each of the individual peaks occurring in the sesquimer-dimer fraction, and A_t is each of the individual peaks occurring in the trimer fraction.

A comparison of the R_{ds-t} values provides a more complete understanding of changes in the polymer structure due to further arrangements in the polymeric chains owing to crosslinking and scission reactions taking place during ageing. Table 3 summarises the average values of R_{ds-t} obtained from three replicates and the corresponding standard deviation. The influence of the amount of sample used for each individual specimen is probably responsible for the different levels of repeatability obtained in the three series of specimens tested. Despite this fact, the results obtained provided us an approach to the changes taking place in the polymer structure during ageing. Thus, the 0.53 value obtained for the unaged resin indicates that a double amount of trimer unities than sesquimer-dimer unities is yielded during pyrolysis. A slightly higher value of 0.59 is obtained for the resin aged by the SO_2 pollutant, whereas a significantly lower value of 0.37 is obtained for the photoaged resin.

Chemical and mechanical changes taking place when Plextol B500 dispersion is led to form a film are similar to those described for other acrylic resins: coalescence of the particles of the polymer suspended in the dispersion, intertwining of polymer chains derived from adjacent particles, and a consequent development of strength owing to the formation of a continuous film. Similarly, an initial period of chemical crosslinking followed by oxidative scission has been reported as one of the most relevant changes taking place during photoageing for ethyl acrylate/methyl methacrylate polymers. This scission breaks down the gel network and results in the formation of shorter polymer segments (Whitmore and Colaluca, 1995). Accordingly, the higher value of R_{ds-t} obtained for the photoaged specimens indicates that a higher level of short segments of polymer is present in the photodegraded resin, resulting in a slight increase of the smaller oligomer unities during pyrolysis. In contrast, the lower value of R_{ds-t} obtained for the specimens aged with the SO_2 pollutant suggests that degradation mechanisms different to those for UV light have taken place in such an instance. The condensation of smaller species to form extended structures or the formation of oxidised polyenes having attached aldehyde, ketone or acid/ester groups, could be on the basis of this different behaviour.

CONCLUSIONS

A synergystic combination of spectroscopic and chromatographic techniques provides a valuable method to study the chemical changes taking place during the ageing of acrylic resins.

Despite the excellent behaviour and high stability exhibited by acrylic resins, remarkable chemical changes have been detected and described in the present study. These being the presence of conjugated chromophores related to the chemical crosslinking responsible for the formation of the polymer film in photoaged Elvacite resins, or the presence of oxidized molecules with aldehyde groups attached in Primal B60 in photoaged specimens.

A comparison of values of the R_{ds-t} parameted proposed in this work enables the recognition of the higher level of short segments of polymer in the photodegraded Plextol B500, whereas a condensation of smaller species to form extended structures or the formation of oxidized polyenes having attached aldehyde, ketone or acid/ester groups, seem to be the degradation mechanisms which take place in specimens aged with the SO_2 pollutant.

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AUTHOR

Mª Teresa Doménech Carbó: Doctor in Chemistry by the University of Valencia. Professor at the Polytechnic University of Valencia.
Professor at the Department of Conservation and Restoration of Cultural Heritage, specialist in chemical and physical analysis of works of art.
Director of the Heritage Conservation Institute of the Polytechnic University of Valencia.

Versión española

TÍTULO: ***Caracterización de cambios en la composición química de las resinas acrilicas envejecidas usadas en arte contemporáneo***

RESUMEN: *Este artículo se centra en el estudio de los cambios en la composición que se producen como resultado del envejecimiento de las resinas acrílicas usadas actualmente en arte contemporáneo, combinando técnicas espectroscópicas de espectrofotometría UV-visible y espectroscopia FTIR y la técnica cromatográfica de pirólisis-cromatografía de gases y espectrometría de masas. Las técnicas instrumentales propuestas se han aplicado sobre una serie de probetas de resinas acrílicas. Se han desarrollado procedimientos de preparación para obtener información relevante sobre los cambios químicos que se producen durante el proceso de envejecimiento acelerado basado en la exposición a la radiación UV y agentes contaminantes, en particular, SO_2.*

PALABRAS CLAVES: *Py-GC-MS, Espectroscopia FTIR, Espectrofotometría UV-VIS, resinas acrílicas, arte*