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Analytical characterization of polymers used in conservation and restoration by ATR-FTIR spectroscopy

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Abstract In the last few decades many new polymers have been synthesized that are now being used in cultural heritage conservation. The physical and chemical properties and the long-term behaviors of these new polymers are determined by the chemical composition of the starting materials used in their synthesis along with the nature of the substances added to facilitate their production. The practical applications of these polymers depend on their composition and form (foam, film, sheets, pressure-sensitive adhesives, heat-seal adhesives, etc.). Some materials are used in restoration works and others for the exhibition, storage and transport of works of art. In all cases, it is absolutely necessary to know their compositions. Furthermore, many different materials that are manufactured for other objectives are also used for conservation and restoration. The technical information about the materials provided by the manufacturer is usually incomplete, so it is necessary to analytically characterize such materials. FTIR spectrometry is widely used for polymer identification, and, more recently, ATR–FTIR has been shown to give excellent results. This paper reports the ATR-FTIR analysis of samples

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of polymeric materials used in the conservation of artworks. These samples were examined directly in the solid material without sample preparation.

Keywords Polymers · ATR-FTIR · Synthetic materials · Restoration and conservation of cultural heritage

Introduction

At present, polymers are very popular and widely available materials. The main reasons for their popularity are the great diversity of synthetic polymers available, the variety of processing techniques that can be applied to them, and the possibility of adding substances to them as they are manufactured. These circumstances are responsible for the use of synthetic polymers in a great number of applications.

There are currently a wide variety of synthetic materials on the market that are utilized within the field of the conservation and restoration of artworks [[1\]](#page-14-0). They are commonly used in packaging, exhibition, handling and storage. In these cases, they act as protectors, supports, and/or thermal and electrical insulators [[2,](#page-14-0) [3\]](#page-14-0). In restoration work, they are used as coatings, adhesives, fixatives, varnishes and consolidants.

Polyolefins, polyesters, polyamides, polyacrylics and polyvinyls are among the most popular of the polymers used in this field, while epoxy polymers are also of interest. Table [1](#page-1-0) shows the structural units of several polymers. The chemical composition of the polymer is responsible for its properties, and it also serves as reference for its analytical characterization by IR spectroscopy.

However, the chemical nature of the polymer is not the only factor that influences its properties and its long-term behavior. Other factors include the molecular size distribution, the degree of crystallinity, and the nature and

proportions of certain materials that are added to the processed polymer as additives, reinforcements and fillers [\[4](#page-14-0)–[6](#page-14-0)]. There are a wide range of these added materials that perform various roles in the final polymer. For example, some are used to increase elasticity, to retard combustion, as antioxidants, as anti-thermal aging factors and UV screens, etc. [\[7](#page-14-0)–[9](#page-14-0)].

One special kind of additives is a foaming or blowing agent, which is added in order to obtain cellular plastics (foams). Cellular plastics have many cavities (cells), and these cells have a certain uniform distribution and size. The cells can be open or closed (Fig. 1). In open-cell plastics, each cell is interconnected with its neighboring cells, or, if it is located at the surface of the cellular plastic, it is open to the external environment. In closed-cell plastics, each cell is fully enclosed, so it is not interconnected with neighboring cells and is not open to the external environment.

Cellular plastics or foams have a number of different characteristics from the noncellular form of the same plastic, such as a lower density and enhanced insulating character [\[10](#page-14-0)].

The was that the polymer is processed is another factor that is directly related to how it is utilized. Various processing methods can lead to films, fibers, foams, corrugated plastics, sheets, multilayers, composites, blends, and reinforcing materials. Multilayered materials can have a corrugated plastic core, a cellular plastic core or a honeycomb core. There are also interesting barrier films in which one of the sheets is made of metal (for example aluminum) [[11\]](#page-14-0).

Most of these materials have not been specifically developed for use in the field of the conservation and restoration of artworks but rather for other industrial applications. Most of them are known by their trade names, which do not tend to be closely related to their compositions. Although manufacturers provide information on the chemical compositions of their products, this information is rarely complete because many of these materials are subject to patents. Thus, it is absolutely necessary to analytically characterize any material that is going to be used in conservation and restoration.

Polymers in art conservation

The term "synthetic polymer" is often associated with perdurability. However, there are cases where the polymer shows chemical and/or physical changes. These changes affect the initial characteristics and sustainability of the material over the long term [[12](#page-14-0)–[15\]](#page-14-0). Some polymers are naturally unstable, such as cellulose derivatives (cellulose nitrate and acetate) and polyurethanes [[16](#page-14-0)–[23\]](#page-14-0).

Ever since the first synthetic and semisynthetic polymers were placed on the market, they have been used by contemporary artists. They also quickly found popularity with conservators (curators) and restorers [\[24](#page-14-0)]. For these reasons, some institutions and agencies responsible for the conservation and restoration of heritage have facilitated the development of work related to the analysis of polymeric materials in works of art and their behavior over the long term. Some examples of these institutions are The Getty Conservation Institute (GCI), The Canadian Conservation Institute (CCI), and The Smithsonian Institute. Also, since the 1980s, some organizations such as the Association Suisse de Conservation et Restoration (SCR), The International Council of Museums—Committee for Conservation (ICOM-CC), and the International Institute for Conservation (IIC) have organized meetings, conferences, congresses and symposia at which these investigations are reported. Numerous publications have resulted from these activities [[25](#page-14-0)–[29](#page-14-0)].

The situation explained above and other polymer studies indicate the importance of having a detailed knowledge of the materials used in the field of conservation and restoration. Because of this, a research project has been launched that aims to investigate the chemical formulations and some of the properties of synthetic materials used in conservation and restoration and their behaviors over the long term.

Fig. 1 Cellular plastics: types of cells. Pictures were obtained from a stereoscopic light microscope. a open cell; b closed cell

The results reported in this paper correspond to an initial stage of work where analytical characterization has been performed for some of the main materials used (mainly) in the context of the preventive conservation of works of art (handling, packaging, exposure). The materials analyzed relate to products with different finishes (foaming, laminated, multilayer and fiber).

Various instrumental analytical techniques have been used to identify polymers and additives [\[30](#page-14-0)–[32](#page-14-0)]. The most useful of these are gas chromatography–mass spectrometry (GC-MS), pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS), direct temperature-resolved mass spectrometry (DTMS), and vibrational spectroscopy techniques (Raman and FTIR).

GC-MS is a separation technique that is used to identify plasticizers in polymers. Py-GC-MS has been applied to the identification of an extensive range of synthetic materials [\[33](#page-14-0)]. In a polymer blend, it is often possible to detect all of the different types of monomers present in the sample. Unlike FTIR, Raman and DTMS, the presence of a signal from an additive does not interfere with the diagnostic peaks. However, it is not possible to carry out a fully quantitative analysis on any of the copolymers or mixed materials because of the occurrence of often quite complex fragmentation reactions during pyrolysis.

Direct temperature-resolved mass spectrometry (DTMS) [\[33](#page-14-0)] is Py-GC-MS without the GC component. This has the advantage of making the technique sensitive to a much wider range of materials, in particular to those that are polar and/or have high boiling points that are unable to pass through a GC column [[34\]](#page-14-0). The disadvantages of DTMS are that the mass spectra of individual molecules can overlap, and that polymer blends yield mass spectra of increased complexity.

There are a variety of techniques that have been used recently to characterize polymeric materials, such as nuclear magnetic resonance (NMR) to measure the relative proportions of each monomer in the acrylic copolymer [\[35](#page-14-0)], sizeexclusion chromatography (SEC) to observe the molecular weight distribution of the polymer and surfactant, and thermogravimetric analysis (TGA) to monitor the insoluble fraction of the polymer (the two last techniques are also used to evaluate changes in polymers upon exposure to light).

The technique most frequently used to identify polymers and additives in plastics is Fourier transform infrared (FTIR) spectroscopy [\[36](#page-14-0)]. The composition of a polymer material can be determined using tables in order to correlate infrared absorption energies with specific chemical bands [\[37](#page-14-0)]. The results can then be compared with commercially available reference libraries or a specifically prepared online spectral database [\[38](#page-14-0)]. There are several examples of the use of this analytical technique to identify synthetic and semisynthetic polymers (binders, adhesives, coatings, supports, etc.) [[39](#page-14-0)–[41](#page-14-0)]. It has also been used to determine changes in the chemical structures of polymers used in restorative treatments [[42](#page-14-0), [43\]](#page-15-0). The benefit of using attenuated total reflectance (ATR) in combination with FTIR for the analysis of polymers has been demonstrated [[15,](#page-14-0) [44\]](#page-15-0).

Raman spectroscopy is an experimental method that is suitable for obtaining structural parameters. It can be used to analyze the chemical substances present in a material; moreover, the chain's orientation, crystallinity and its evolution during the aging process can be obtained. Although the use of Raman spectroscopy to study polymers has been limited in the past due to sample fluorescence, the emergence of FT-Raman spectroscopy has resulted in the succesful use of this technique to investigate polymers. FT-Raman and FTIR spectra provide similar (but not identical) information (weak FTIR absorptions are usually strong in FT-Raman and vice versa), so the two techniques are complementary. FT-Raman has been used to study synthetic and semisynthetic polymers [\[45](#page-15-0), [46](#page-15-0)]. One disadvantage is the fluorescence that appears in samples with impurities or in industrial materials [\[47](#page-15-0)].

In this work, the analytical technique used was ATR-FTIR spectroscopy. This allowed the polymers or polymer blends present in the materials under investigation to be identified. It was also possible to characterize the fillers and other additives used when processing polymeric materials. It is an ideal technique for the analysis of plastic materials.

Experimental

Samples

The materials analyzed included adhesives, nonwoven fabrics, supports, insulating materials and foams. Some of them are polymer blends and composite materials. Table [2](#page-4-0) shows the materials analyzed in this work.

Instrumentation

A Fourier transform infrared spectrometer (Thermo Nicolet 380) with a DTGS (deuterated triglycine sulfate) temperature-stabilized coated detector was used (4000– 400 cm−¹). This was equipped with an attenuated totalreflection diamond crystal accessory (ATR). The spectra were obtained in absorbance mode from 64 scans at 4 cm⁻¹ resolution. The spectra were analyzed using Omnic v 7.3 and processed with Origin v 7.0.

A stereoscopic light microscope (Leica MZ125) was used for morphological examinations of the materials and to select the samples for analysis. It also allowed us to distinguish the different layers in the multilayer materials analyzed.

Table 2 Synthetic polymers analyzed in this work

^aThis material is supplied by Productos de Conservación (Spain). It is a polyester. There is also another material with the same name (manufactured by Ten Cate) and made from UV-stabilized poly(propylene)

Procedure

ATR-FTIR analytical characterization was performed for polymer identification. Sample analysis is performed directly using ATR-FTIR; there is no preparation of samples. The analysis is superficial and the depth corresponding to the spectral region covered is less than 4 μm; therefore, if the material is two-sided it will be necessary to carry out the analysis on both sides. The quality of the spectrum depends on intimate contact between the diamond crystal and the sample. This effect is achieved through the use of a high-pressure clamp.

A prior morphological exam was performed in all cases. For the cellular plastics, testing included examining the cell type (open or closed).

The obtained ATR-FTIR spectra were interpreted with respect to the bands from the polymers in the analyzed material. When additives were present in the material, they were identified via the bands from the characteristic groups of these components. Finally, the spectra obtained were compared with those of polymers and reference libraries of additives.

Results and discussion

Fifteen samples were studied in this work. Previous studies [\[2](#page-14-0), [3,](#page-14-0) [48](#page-15-0)] were consulted, along with the information obtained by the manufacturer. The samples were classified according to the chemical nature of the polymer, the type of processing applied to it, and practical applications of it. The initial study was completed along with a morphological examination. This allowed the type of material to be assessed; for example, whether it was a nonwoven fabric, a foam, a multilayer or a composite material.

Morphological examinations of Marvelseal®, Tyvek® tape and Lampraseal® confirmed that they were multilayer composite materials and located their layers. Morphological examinations of Cell-Aire®, Ethafoam®, Plastazote® and the poly(ethylene) rod indicated that they were cellular plastics or foams. Closed cells were observed in Cell-Aire®, Ethafoam®, and Plastazote®, while there were open cells in the poly(ethylene) rod. The morphology of the material influences its subsequent use in the conservation of artworks. Properties such as resilience, thermal insulation and mechanical insulation (from vibrations) will differ between open and closed cell foams. Closed cell foams exhibit better thermal insulating behavior than open cell foams.

Another cellular plastic is foam core board. It is made by adhering two sheets of paperboard to both sides of a foam core, creating a multilayer compound material. Morphological examination of the foam core indicated the presence of closed cells.

Table [3](#page-5-0) summarizes the main ATR-FTIR absorption bands of the samples analyzed in this study.

The foam materials are commonly used to make padding supports in storage, mounts and packaging. They can be

Trade Name	Polymer Type	Main IR absorption bands used for identification $(cm-1)$
Cell-Aire®. Plastazote®, Ethafoam [®] . Polyethylene rod	Low-density poly(ethylene), LDPE	$v_{asymmetric}$ and $v_{symmetric}$ –CH ₂ – (2915 and 2845) δ _{asymmetric} in plane and δ symmetric in plane C-H (1470 and 1377) δ_{rocking} C-H (-CH ₂ -) _{n≥6} (717)
Lampraseal®	Low-density poly(ethylene), LDPE (plastic layer: smooth side)	$v_{asymmetric}$ and $v_{symmetric}$ -CH ₂ - (2917 and 2844) δ _{asymmetric} in plane and δ symmetric in plane C-H (1467 and 1375) δ_{rocking} C-H (-CH ₂ -) _{n≥6} (717)
	Poly(propylene) (fiber side: nonwoven fabric)	$v_{\text{asymmetric}}$ and $v_{\text{symmetric}}$ –CH ₃ (2950 and 2867) $v_{\text{asymmetric}}$ and $v_{\text{symmetric}}$ –CH ₂ (2917 and 2838) $VC-H_{\text{methvlene group}}(2875_{\text{shoulder}})$ δ _{asymmetric in plane} and δ symmetric in plane C-H (-CH ₂) (1455 and 1358 _{shoulder}) δ _{asymmetric} in plane and δ _{symmetric} in plane C-H (-CH ₃) (1436 shoulder and 1375) $\delta_{\rm rocking}$ –CH ₃ and vC-C (1166 and 972) δ_{rocking} and δ_{wagging} –CH ₂ (997) vC-C (polymer backbone) (1153 _{shoulder} and 808) $\delta_{\text{rocking}} - \text{CH}_2$ - (898 and 840)
Marvelseal [®]	Poly(ethylene vinyl acetate), EVA (heat seal side)	$v_{asymmetric}$ and $v_{symmetric}$ –CH ₂ – (2915 and 2848) $v = O_{\text{ester}} (1740)$ δ _{asymmetric} in plane and δ symmetric in plane C-H (1470 and 1370) $V[C-C(O)-O]$ (1239) $v[-O-C-](1020)$ δ_{rocking} C-H (-CH ₂ -) _{n≥6} (718)
	Polyamide (glossy side)	v –NH (3300) Amide II overtone (3078) $v_{asymmetric}$ and $v_{symmetric}$ –CH ₂ – (2931 and 2860) Amide I (v C=O) (1637) Amide II (δ _{in plane} –NH and v C-N) (1537) δ _{asymmetric in plane} and δ _{symmetric} in plane C-H (1462, 1438, and 1371) $\delta_{\text{in plane}}$ –CH ₂ – [–CH ₂ –(NH–)] (1474 _{shoulder}) $\delta_{\text{in plane}}$ –CH ₂ – [–CH ₂ –(CO–)] (1417) Amide III (v C-N and $\delta_{\text{in plane}}$ –NH) (1260) $\delta_{\text{out of plane}}$ C-H (1198 and 1169) Amide V ($\delta_{\text{out of plane}}$ N– H) (729) Amide IV [δ – C(O) – N– H] (678)

Table 3 ATR-FTIR absorption bands associated with the analyzed materials, and the polymers identified in them

Table 3 (continued)

Table 3 (continued)

Table 3 (continued)

processed as films, sheets or rods. The foam materials that were analyzed were Plastazote®, Ethafoam®, Cell-Aire® and a poly(ethylene) rod. Their spectra were similar. The Cell-Aire® ATR-FTIR spectrum (Fig. 2) shows various characteristic bands: v_{as} and v_{s} –CH₂– (2915 and 2845 cm⁻¹), δ_{as} and $\delta_{\text{s in plane}}$ C-H (1470 and 1377 cm⁻¹), and $\delta_{\text{rocking}}C - H(-CH_2-)_{n \ge 6}(717 \text{ cm}^{-1})$. Thus, it is a low-density poly(ethylene) (LDPE).

Multilayer materials are commonly used for support and packing. The materials analyzed were Lampraseal® and Marvelseal®. Lampraseal® has two layers: a plastic layer (smooth side) and a nonwoven fabric (fiber side). The spectrum of the plastic layer (Fig. [3a\)](#page-9-0) corresponds to low-density poly(ethylene) (LDPE): v_{as} and v_s −CH₂− (2917 and 2844 cm⁻¹), δ_{as} and δ_{s} _{in-plane} C–H (1467 and 1375 cm⁻¹), and δ_{rocking}C – H(−CH₂−)n ≥ 6(717 cm⁻¹). The nonwoven fabric spectrum (Fig. [3b\)](#page-9-0) shows the bands of poly(propylene), specifically that of the isotactic

conformer [[49](#page-15-0)]: v_{as} and v_{s} –CH₃ (2950 and 2867 cm⁻¹), v_{as} and v_{s} -CH₂- (2917 and 2838 cm⁻¹), v C-H _{methyne} group (2875 cm⁻¹), δ_{as} and δ_{s} in-plane C-H (-CH₂-) (1455 and 1358 cm⁻¹), δ_{as} and δ_{s} in-plane C-H (−CH₃) (1436 and 1375 cm⁻¹), δ_{rocking} –CH₃ and γ C–C _{polymer backbone} (1166 cm⁻¹ and 972 cm⁻¹), δ_{rocking} –CH₃ and δ_{wagging} −CH2− (997 cm−¹). Other features in the fingerprint region are: $\sqrt{C-C}$ polymer backbone (1153 and 808 cm⁻¹) and δ_{rocking} $-CH_2$ (898 and 840 cm⁻¹).

Marvelseal[®] is a vapor barrier. According to the manufacturer, it is an aluminized poly(ethylene) and nylon barrier film. It resists the transmission of water vapor and other atmospheric gases, so it is a multilayer compound material. One of the sides serves as a heat seal adhesive. The ATR-FTIR spectrum (Fig. [4a](#page-9-0)) shows bands corresponding to: v_{as} and v_{s} –CH₂– (2915 and 2848 cm⁻¹), γ C=O_{ester} (1740 cm⁻¹), δ_{as} and $\delta_{\text{s in-plane}}$ C-H (1470 and 1370 cm⁻¹), γ [C−C(O)−O] (1239 cm⁻¹), γ [−O−C−] (1020 cm⁻¹), and δ_{rocking} C – H(–CH₂–)n $\geq 6(718 \text{ cm}^{-1})$. These bands correspond to poly(ethylene vinyl acetate) (EVA). The spectrum of the other side is very different (Fig. [4b](#page-9-0)). The most significant bands are: ν -NH (3300 cm⁻¹), amide I (ν C=O) (1637 cm⁻¹), amide II (δ _{in-plane} -NH and ν C-N) (1537 cm⁻¹), and amide III (ν C−N and $\delta_{\text{in-plane}}$ -NH) (1260 cm−¹). It also shows bands corresponding to: amide II overtone (3078 cm⁻¹), v_{as} and v_{s} -CH₂- (2931 and 2860 cm⁻¹), δ_{as} and δ_{s in-plane} -CH₂- (1462, 1438 and 1371 cm⁻¹), δ_{in-plane} - CH₂ − [-CH₂ − (NH−)] (1474cm⁻¹), $δ_{in-plane}$ ⁻CH₂⁻[⁻CH₂⁻(CO⁻)] (1417 cm⁻¹), $δ_{out-of-plane}$ C-H (1198 and 1169 cm⁻¹), amide V (δ _{out-of-plane} N-H) (729 cm⁻¹), and amide IV (δ [-C(O)-N-H]) (678 cm⁻¹). So this spectrum clearly corresponds to the reference spectrum of a polyamide.

Some polymers are used as pressure-sensitive adhesives Fig. 2 ATR-FTIR Cell-Aire® spectrum (PSA). Such adhesives are materials that are aggressively and

Fig. 3 a ATR-FTIR spectrum of the smooth side of Lampraseal®. b ATR-FTIR spectrum of the fiber side of Lampraseal®

permanently tacky at room temperature and firmly adhere to a variety of dissimilar surfaces upon further contact without the need for more than finger or hand pressure. Such materials must have low glass transition temperatures (T_{α}) .

The Tyvek® tape (DuPont) is a pressure-sensitive adhesive. It is used to bind folder spines, to repair battered books, as well as for a variety of other applications. Both sides of the tape were analyzed: the support and the adhesive. The ATR-FTIR spectrum of the support (Fig. [5a\)](#page-10-0) shows characteristic bands corresponding to v_{as} and v_{s} −CH₂− (2913 and 2847) cm⁻¹), δ_{as} and δ_{s} in-plane C-H (1471 and 1462 cm⁻¹), and $\delta_{\text{rocking}}C - H(-CH_2-)$ n $\geq 6(730 \text{ and } 717 \text{ cm}^{-1})$. This spectrum clearly corresponds to the reference spectrum of high-density poly(ethylene) (HDPE).

The spectrum of the adhesive side of the tape (Fig. [5b\)](#page-10-0) shows characteristic bands corresponding to an acrylic polymer, poly $(n$ -butyl acrylate) [[50](#page-15-0)]. Its functional ester group $\left[-C(O)-O-(CH_2)_3CH_3\right]$ is a branch of the polymer backbone $[-CH_2-CH-]$ (Table [1](#page-1-0)). The bands that correspond to the ester group are: \sqrt{C} C=O_{ester} (1728 cm⁻¹),

 γ [C–C (O)–O] (1241 cm⁻¹) and γ [-O–C–] (1158 cm⁻¹). Other interesting bands are associated with vibration modes of the C−H bonds in the polymer backbone and the alkyl groups of the branched chains. These are: v_{as} and v_{s} −CH₃ (2959) and 2869 cm⁻¹), v_{as} and v_{s} -CH₂- (2914 and 2847 cm⁻¹), ν CH_{methyne group} (2930 cm⁻¹), δ_{as} and δ_{s} _{in-plane} -CH₂-_{n-butyl} group (1447 and 1395 cm⁻¹), δ in-plane $-CH_2$ ⁻polymer backbone (1461 cm⁻¹), overlapping $\delta_{\text{in-plane}}$ –CH₂-support (HDPE), and $\delta_{\rm s}$ in-plane $\rm{-CH_3}$ n-butyl group (1379 cm⁻¹). Other bands in the fingerprint region have also been assigned: $\delta_{\text{out-of-plane}}$ C−H_{n-butyl} group and γ C−C_{polymer main chain} (1116, 960 and 940 cm⁻¹), $\delta_{\text{out-of-plane}}$ C−H_{n-butyl} group (1065 and 848 cm⁻¹), γ C−C_{polymer main chain} (1024 cm⁻¹), and δ_{rocking} (−CH₂−) (731 and 716 cm−¹).

The adhesive spectrum shows absorption bands that correspond to the reference spectrum of $poly(n$ -butylacrylate) and support characteristic traces. The bands that indicate that the adhesive is contaminated with HDPE are the doublet at 731 and 716 cm^{-1} and the bands in the region of C−H stretching and deformation vibrations (Fig. [5b](#page-10-0)).

Fig. 4 a ATR-FTIR spectrum of the heat-seal side of Marvelseal®. b ATR-FTIR spectrum of the glossy side of Marvelseal®

Fig. 5 a ATR-FTIR spectrum of the support side of the Tyvek[®] tape. b ATR-FTIR spectrum of the adhesive side of the Tyvek® tape. Asterisks, bands associated with the support side

Acrylate esters of C_4-C_{12} alcohols comprise the major constituent of the PSA. These give homopolymers with T_{g} of about −50 °C to −75 °C [[51](#page-15-0)]. According to the information obtained by ATR-FTIR, the Tyvek® tape adhesive is poly (*n*-butyl acrylate). This acrylic presents a T_g of −54 °C [\[1](#page-14-0)].

Heat-seal adhesives are also very interesting. This group includes Beva® film 371, which is used in painting linings, to fix pictorial layers, and to apply patches and borders. The Beva® 371 adhesive was developed by G. Berger and is a mixture of a combination of ethylene vinyl acetate (EVA) resins with a variety of waxes and ketone resins [[52\]](#page-15-0). The ketone resins are obtained by the polymerization of cyclohexanone. The final product (comprising six units) has been found to possess one carbonyl, one methoxy, one other ether group, and three hydroxyl groups [[53,](#page-15-0) [54](#page-15-0)].

The ATR-FTIR spectrum of Beva® 371 film (Fig. 6) shows bands corresponding to poly(ethylene vinyl acetate) (EVA): v_{as} and v_{s} –CH₂– (2917 and 2849 cm⁻¹), v C=O_{ester} (1736 cm⁻¹), δ_{as} and δ_{s} in-plane C−H (1467 and 1375 cm⁻¹),

 ν [C-C(O)-O] (1242 cm⁻¹), ν [-O-C-] (1024 cm⁻¹), and $\delta_{Rocking}C - H(-CH2-)N \geq 6(720 \text{ cm}^{-1})$. Bands that correspond to a ketone resin [poly(cyclohexanone)] have also been identified: ν OH (3500–3200 cm⁻¹), ν C=O _{ketone} (1713 cm⁻¹), $\delta_{\text{in-plane}}$ C-H cyclohexanone (1451 cm⁻¹), γ C-O methoxy, $\delta_{\text{in-plane}} C = O_{\text{ketone}}$ and $\delta_{\text{out-of-plane}} C$ −H (1122 cm⁻¹), γ C−O _{hydroxyl} and δ [−C−(CO)−C−]_{cyclic ketone} (1058 cm⁻¹) and $\sqrt{C-C_{\text{backbone}}}\$ cyclic structure (960 cm⁻¹).

Archibond is another heat-seal adhesive used in textile and fan restoration, in documentary and graphic work restoration, and for mounting ex libris, illustrations, etc. There are different types of Archibond: Archibond tissue, Archibond without support, and Archibond fiber. All of these consist of an adhesive over a variety of supports. The type studied in this work is Archibond without support. The adhesive is placed between two silicon papers. The adhesive was separated from the substrate in order to carry out the ATR-FTIR analysis. Figure [7](#page-11-0) shows the spectrum of the adhesive of Archibond. When this is compared with the reference spectrum of Paraloid B72, both spectra are clearly similar.

Paraloid B-72 is a commercial synthetic polymer that is used in restorative treatments as a coating, consolidant and adhesive. It is a copolymer of ethyl methacrylate and methyl acrylate.

Bands identified in the Archibond spectrum include: v_{as} and v_s –CH₃ (2982, 2951 and 2874 cm⁻¹), v_{as} and v_s –CH₂– (2907 and 2850 cm⁻¹), γ CH_{methyne group} (2929 cm⁻¹), γ C=O_{ester} (1721 cm⁻¹), δ_{as} and δ_{s} in-plane C−H (−CH₂ −) (1471 and 1384 cm⁻¹), δ_{as} and $\delta_{\text{s in-plane}}$ C−H (−CH₃) (1446 and 1367 cm⁻¹), γ [C-C(O)-O] (1233 cm⁻¹), γ [-O-C-] (1140 cm⁻¹), δ_{rocking} –CH₃ and δ_{wagging} –CH₂– (1022 cm⁻¹), and δ_{rocking} –CH₂– (858 and 753 cm⁻¹).

There are different materials that have the same composition but that are used for different purposes in conservation and restoration. Melinex® and Polyfelt are

Fig. 6 ATR-FTIR spectrum of Beva® 371 film. Asterisks, bands belonging to poly(cyclohexanone)

Fig. 7 ATR-FTIR spectrum of Archibond

examples of this; these materials have the same polyester composition. Melinex® takes the form of a film. The thickness of the film determines its practical applications. It is an isolating material that is used in paper and photographic conservation. Polyfelt is a nonwoven fabric used in packing as a soft protector and isolator.

Figure 8 shows spectra for Melinex® and Polyfelt. The bands assigned to Melinex[®] are: γ C=O_{ester} (1713 cm⁻¹), γ [C−C (O)−O] (1240 cm⁻¹) and γ [−O−C−] (1120 and 1098 cm−¹). Bands are also observed at 2965, 2923, 2908 and 2853 cm^{-1} , and these are associated with stretching vibrations of the backbone polymer (v_{as} and v_s −CH₂−). Bands are also observed at 1470, 1410, 1372 and 1340 cm−¹ , which correspond to deformation bands (δ _{as} and δ _{s in-plane} C−H); δ _{rocking} C−H (−CH₂)− (847 cm−¹) was also identified. Other interesting bands are associated with C=C and C−H bonds of the aromatic ring. These bands are: \sqrt{C} C=C (1615, 1580 and 1505 and 1454 cm⁻¹), $\delta_{\text{in-plane}}$ =C−H (1016 and 970 cm⁻¹), $\delta_{\text{out-of-plane}}$ =C−H (870 cm⁻¹)

Fig. 8 ATR-FTIR spectra of Melinex[®] and Polyfelt hydroxy-4-(n-octyloxy) benzophenone

and δ_{wagging} =C−H (720 cm⁻¹). Note that the ATR-FTIR spectra of both Polyfelt and Melinex® are similar and show characteristic bands corresponding to the same polyester, poly(ethylene terephthalate) (see Fig. 8 and Table [3](#page-5-0)).

Corrugated plastics are used as supports and to enclose objects. The corrugated materials analyzed here were Lexan®, Coroplast® and Polyonda®. The plastic were analyzed both internally and externally in all three cases.

According to the manufacturer' description, Lexan® is a cellular polycarbonate sheet. However, the results obtained demonstrate that it is a compound material that is processed into a corrugated multilayer material with a plastic core. The internal ATR-FTIR spectrum shows

Fig. 9 a Internal ATR-FTIR spectrum of Lexan®. b ATR-FTIR spectrum of the exterior of Lexan®. Asterisks, bands belonging to 2-

characteristic bands corresponding to an aromatic polycarbonate (Fig. [9a](#page-11-0)). The most significant bands are: ν C=O (1768 cm⁻¹), ν [O-C(O)-O] (1218, 1186 and 1158 cm⁻¹) and γ [-O-C-] (1013 cm⁻¹), which are associated with the carbonate group [O−C(O)−O]. Other bands of interest are those that correspond to the aromatic ring: ν =C−H (3057 and 3040 cm⁻¹), ν C=C (1593, 1503 and 1454 cm⁻¹), $\delta_{\text{in-plane}} = C-H$ (1102 cm⁻¹), $\delta_{\text{out-of-plane}} =$ C−H (886 cm⁻¹) and δ_{wagging} =C−H (828 cm⁻¹). The bands of the methyl and methylene groups are also important: v_{as} and v_s −CH₃ (2966 and 2872 cm⁻¹), v_{as} and v_s −CH₂− (2929 and 2853 cm⁻¹), δ_{as} and δ_{s} _{in-plane} C−H (−CH₂−) (1464 and 1364 cm⁻¹), and δ_{as} and δ_{s} in-plane C−H (−CH₃) $(1409 \text{ and } 1386 \text{ cm}^{-1}).$

The spectrum of the exterior of Lexan® presents significant differences from the internal spectrum of Lexan® regarding the absorption bands and the frequencies at which they appear (Fig. [9b](#page-11-0)). It shows the characteristic bands of an acrylic polymer, specifically poly(methyl methacrylate). The functional group of this polymer, the ester $[-C(O)-O-CH_3]$, is a brach of the polymer backbone $[-CH_2-C(CH_3)-]$ (Table [1](#page-1-0)). In addition to the bands from the methyl (−CH₃) and methylene (−CH₂−) groups; i.e., v_{as} and v_{s} (−CH₃) (2993 and 2926 cm⁻¹), v_{as} and v_s (−CH₂−) (2949 and 2852 cm⁻¹), δ_{as} and δ_{s} _{in-plane} (−CH₂−) (1480 and 1434 cm⁻¹), and δ _{as} and δ _{s in-plane} $(-CH₃)$ (1446 and 1381 cm⁻¹), bands that fit the ester group have been identified: \sqrt{C} C=O_{ester} (1723 cm⁻¹); $\sqrt{C-C}$ (O)−O] (1239 cm⁻¹), and γ [-O-C-] (1189 and 1143 cm⁻¹). There are also other bands, which have been assigned to the following groups: ν C=C aromatic ring (1620, 1597 and 1575 cm⁻¹), δ [C_{aromatic ring}-O-C] (1343 cm⁻¹), δ_{out-of-plane} C−H_{aromatic ring} (915 cm⁻¹), δ_{wagging} C−H_{aromatic ring} (810 and 825 cm⁻¹), δ_{rocking} C−H (−CH₂−)_{n≥6} (700 cm⁻¹), and δ_{in-plane} [C_{aromatic ring}-C(O)] (630 cm⁻¹). Based on this information, and after comparing the spectrum obtained here with the corresponding reference spectrum, it was deduced that the poly(methylmethacrylate) contains an aromatic additive, probably 2-hydroxy-4-(n-octyloxy)-benzophenone. This additive acts as a UV absorber, improving its behavior upon exposure to light [\[55\]](#page-15-0).

According to the manufacturer, Coroplast® is an extruded twin-walled poly(propylene) copolymer. In terms of its processing, it is a corrugated sheet. The ATR-FTIR spectra for the external and internal sides of Coroplast[®] are the same, so they have the same composition: a polymer blend with an additive filler (Fig. 10). The bands identified are: v_{as} and v_{s} –CH₃ (2950 and 2867 cm⁻¹), v_{as} and v_s –CH₂– (2916 and 2838 cm⁻¹, γ C–H_{methyne} group (2875 cm⁻¹), δ_{as} and δ_{s} in-plane C−H (−CH₂−) (1456 and 1358 cm⁻¹), δ_{as} and δ_{s} in-plane C−H (−CH₃) (1434 and 1375 cm⁻¹) and δ_{rocking} –CH₃ and γ C–C (1166 cm⁻¹ and 973 cm⁻¹), δ_{rocking} – $\overline{\text{CH}}_3$, and δ_{wagging} – CH_2 – (998 cm⁻¹).

Fig. 10 ATR-FTIR spectrum of Coroplast®. Asterisks, bands belonging to talcum

Other features have also been identified in the fingerprint region: $\sqrt{\text{C}-\text{C}}_{\text{backbone}}$ polymer (1153 and 808 cm⁻¹) and δ_{rocking} –CH₂– (898 and 840 cm⁻¹). Based on this information and reference spectra, we deduced that Coroplast® is a polymer blend: poly(propylene) mixed with poly(ethylene propylene). The bands from the additive filler appear at 1017, $675, 536, 463$ and 451 cm^{-1} , and are identical to those of talcum. Thus, this compound is added as filler.

Polionda® (Fig. [11](#page-13-0)) is a corrugated sheet. Its internal and external spectra correspond to a polymer blend of the same composition as that of Coroplast®. It is made by mixing poly (propylene) with poly(ethylene propylene). But in this case no additive was identified. The bands identified are: $v_{\rm as}$ and $v_{\rm s}$ –CH₃ (2949 and 2863 cm⁻¹), $v_{\rm as}$ and $v_{\rm s}$ –CH₂– (2917 and 2837 cm⁻¹, γ C-H _{methyne group} (2875 cm⁻¹), δ_{as} and $\delta_{\rm s}$ in-plane C−H (−CH₂−) (1455 and 1358 cm⁻¹), $\delta_{\rm as}$ and $δ$ _{s in-plane} C−H (−CH₃) (1434 and 1375 cm⁻¹), $δ$ _{rocking} −CH₃ and ν C−C (1168 and 972 cm⁻¹), ν C−C (backbone polymer) (1153 and 808 cm⁻¹), δ_{rocking} –CH₃ and δ_{wagging} $-CH_2$ – (997 cm⁻¹), and δ_{rocking} – CH₂– (900 and 841 cm⁻¹).

Finally, a foam core board was analyzed. This is a special multilayer material with a cellular plastic (foam) core. It is made by adhering two sheets of paperboard to both sides of a foam core. It is a lightweight yet sturdy material that is ideal for all indoor mounting applications and is used as artwork backing, for photographic mounting, for framing, etc. The FTIR-ATR spectrum of the foam shows a clear correspondence to polystyrene (Fig. [12a\)](#page-13-0). The bands identified are: ν =C–H_{aromatic ring} (3081, 3059, 3024 and 3001 cm⁻¹), ν_{as} and v_s –CH₂– (2919 and 2847 cm⁻¹), overtones that indicate monosubstituted aromatic rings (1940, 1868, 1800 and

Fig. 11 ATR-FTIR spectrum of Polionda®

1743 cm⁻¹), \sqrt{C} C=C_{aromatic ring} (1601, 1583, 1492 and 1451 cm⁻¹), δ_{as} and δ_{s in-plane} C−H (−CH₂−) (1372 and 1311 cm⁻¹), $\delta_{\text{in-plane}} = \stackrel{\frown}{C} - H$ (1180, 1154, 1068 and 1027 cm⁻¹), δ _{out-of-plane} = C−H (905, 840 and 749 cm⁻¹), and $\delta_{\text{out-of-plane}}$ from the aromatic ring (694 and 537 cm⁻¹).

Both sides of the paperboard were coated with a smooth surface film. This surface was analyzed by FTIR-ATR and exhibited a complicated spectrum. An adhesive and two additive fillers were identified (Fig. 12b). The bands that correspond to the adhesive are: v_{as} and v_{s} −CH₂− (2920) and 2853 cm⁻¹), γ C=O_{ester} (1737 cm⁻¹), δ _{s in-plane} C-H (−CH₂−) (1375), and γ [−C−C (O)−O] (1242 cm⁻¹). The other stretching vibration that is characteristic of the ester group, γ [-O-C], occurs at ca. 1020 cm⁻¹, but overlaps with a band assigned to one of the additive fillers. These bands correspond to poly(vinyl acetate).

The additive fillers are calcite $(CaCO₃)$ and kaolin [aluminium silicate hydroxide−Al₂Si₂O₅(OH)−]. The former (CaCO₃) has a strong broad band at 1418 cm⁻¹ and a sharp band of medium intensity at 874 cm⁻¹. Like most clays, kaolin shows bands at 3688, 3647 and 3618 cm^{-1} . They are exhibit characteristic bands at 1113, 1026, 1001, 935, 911, 792, 751, 680, 527, 463 and 428 cm⁻¹.

Kaolin is mainly used as a filler and a coating in paper production that ensures that some grades of paper are glossy.

Conclusions

ATR-FTIR spectroscopy is an analytical technique that is very useful for analyzing synthetic polymers used in conservation and restoration.

In accordance with the results presented in this paper, this technique allows the analysis of materials made of synthetic polymers that have different chemical characteristics and have been subjected to different types of processing. Films such as Melinex®, foam films such as Cell-Aire®, nonwoven fabrics

such as Polyfelt, and adhesives such as Archibond have been characterized. This analytical technique also gave good results in the characterization of polymer blends (BEVA® film, Coroplast® and Polionda®).

It is a superficial analysis technique, so it only provides information on the surface of the material being analyzed. Therefore, when multilayered composite materials are being analyzed, it is necessary to carry out the analysis on all of the layers. In the case of composite materials with

Fig. 12 a ATR-FTIR spectrum of the foam of the foam core board. **b** ATR-FTIR spectrum of the board of the foam core board. Asterisks, bands that correspond to poly(vinyl acetate). Crosses, bands that correspond to calcite. Dots, bands that correspond to kaolin

more than two overlapping layers, this technique does not allow information on the internal layers to be obtained, and so it is necessary to separate out the layers of the material and analyze each component. The results obtained in layered composite materials like Marvelseal® were found to be in good agreement with the manufacturer's specifications. However, the information obtained for Lexan® and the foam core board were not provided by the manufacturers of these materials.

ATR-FTIR has also allowed the identification of additives that are present in some of the studied materials, including additive fillers (Coroplast® and foam core board) and UV absorbers (Lexan®).

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