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Binary mixtures of ethylene containing copolymers and low molecular weight resins: a new approach towards specifically tuned art conservation products.

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Key words

Heat seal adhesives, ethylene-based copolymers, , conservation, consolidating adhesives

Abstract

Painted face artworks often require adhesives during their conservation treatment. Damage or ageing processes that result in cracking, powdering, lifting or similar phenomena can occur, at the interface between two paint layers or between a paint layer and the support. Adhesives need to be applied without compromising the original appearance of the object. Those products can either be formulated to provide structural strength at the interface or be applied more diluted, so that they can penetrate into a weakened porous material to improve cohesive bulk properties strength. In the latter case the adhesive is typically referred to as a consolidant.

Since this is a niche sector, only a few formulations are tailored specifically for restoration, while almost all products used are transposed from various commercial fields. Furthermore the notion of reversibility limits the range of polymeric materials for conservation to chemically stable thermoplastics, because they can be safely removed.

This paper introduces the results of an international project which aims at characterizing the behaviour of new adhesive formulations with tuned physicochemical properties and enhanced stability. These are

binary mixtures, based on ethylene copolymers and four classes of tackifier. On the contrary of urea-aldehyde and hydrogenated hydrocarbon resins, ketone and rosin ester resins showed good miscibility with the polymeric component. Nevertheless, all tackifiers investigated were able to modify copolymers properties.

1. Introduction

The segment of research introduced here is focused on the development of new thermoplastic polymer based formulations tailored for the needs of the art conservation field.

In general, it can be said, that synthetic polymers entered into the cultural heritage world from the moment they were produced. Used by the artists to create their works of art, they have been employed also as a mechanical part of it (e.g. joints, glue, etc.). In the past decades, polymers have also been used by art conservators as adhesives, consolidants, protective coatings and cleaning materials [1].

Thermoplastic adhesives based on acrylates and methacrylates, vinyl acetate (PVAc) and ethylene vinyl acetate (EVAc) copolymers were introduced in the conservation field in the middle of the last century. Their use has been either limited or encouraged, based on the studies about their reversibility, compatibility and stability [2].

Gustav Berger, a civil engineer who started to work in the conservation field collaborating with conservators, developed in the 1960s one of the few products specifically tuned for works of art [1]. Before arriving at what is known as BEVA® 371 “original formula” (O.F.), he has tested almost three hundreds formulations [3], employing as main constituent polystyrene or ethylene vinyl acetate copolymer shortly after EVAc copolymers were introduced [4]. Before reaching the final formulation, Berger studied the chemical-physical properties and, to a more limited extent, the chemical stability through natural and artificial ageing [4].

BEVA® 371 is best classified as heat seal adhesive (HSA), made out of five components. It contains two EVAc, Elvax® 150 (DuPont™) and A-C® 400 (Honeywell) with a VAc content of approximately 33% and 15%, respectively; the first one chosen because it forms low viscosity solutions. It also contains two tackifiers: Laropal® K80 (BASF) and Cellolyn™ 21 (Eastman Chemical Company, primarly Hercules), and an oil free paraffin wax, which in addition to improving low temperature tack helps ensures "it will stay removable forever" [4]. Naptha, toluene and other aromatic solvents are listed as solvents; however now it is known generally to be a mixture of aromatic and aliphatic solvents.

The original purpose of this product was for the application in lining conservation treatments of paintings on canvas, but it is also employed as a consolidant when depletion occurs [5], whether it be between layers or within the paint film.

Several studies have compared BEVA®371 with other EVAc-based adhesives (e.g. Lascaux 375), confirming its ideal properties as a lining material (thermal and chemical stability) [6-8]. Hartin, et al. [9] underlined the role of temperature and thickness of the adhesive layer on the strength of the bond between the two surfaces in contact: it is stated, BEVA®371 needs to be heated to 65°C after being applied and kept under pressure for at least 1h[10] in order to obtain and reach a suitable bond strength between the original and new canvases.

In 2008 BASF, the manufacture of Laropal® K80, discontinued this ketone resin tackifier, and the manufacturer of BEVA®371 opted for an aldehyde ketone resin as a replacement; the new formulation was renamed BEVA®371b [11]. Conservators like BEVA®371 because it dries matte, "sticks to everything" and can be heated multiple times to adjust previous restorations. Through the use of heat or solvents its viscosity can be modified to control penetration into paint layers and the supports [12]. Although the company claims that the new adhesive is equivalent to the previous one (solubility, activation temperature, adhesion properties, peel strength, reversibility and stability), conservators have complained that it is less "tacky" [13], and empirical experience indicate some subtle differences;

moreover mechanical testing has suggested that more than the composition has changed. The chemical stability has been studied [5], revealing a combination of phenomena which leads to the degradation of this adhesive. The most unstable component in the original formula and in the new one is the main tackifier: ketone resins oxidize rapidly resulting in a change of polarity and solubility as well as yellowing [14-16]. The EVAc copolymers in accelerated light and oxidizing conditions are shown to undergo a slight reduction of molecular weights [5] and loss of acetate groups [17]; compounds that can be potentially dangerous for art materials due to the consequent formation of acetic acid, although this degradation phenomenon occurs on larger time scale.

Stability and reversibility are two of the pursued requirements for products to be applied in art conservation. Therefore, one of the aims of this research project is to develop a new consolidating adhesive, specifically tuned for painted cultural objects. The first step is the characterization of binary mixtures made with a base copolymer and a tackifier. These types of blends are different from the commercial formulations and there are no studies related to their possible application in the conservation field. Like for the EVAc, the degradation of ethylene-acrylate copolymers has been studied as well, and their best chemical stability has been reported [17,18]. Not only does the degradation occur only after extensive ageing, but they release mainly carbon dioxide and alcohols, which are non-reactive towards artistic media.

For this reason, EVAc-based blends, although already studied by several researchers [19-26], are compared here with adhesive systems based on ethylene butyl acrylate (EBA) copolymers. These macromolecules were developed in order to address the deficiencies of EVAc [27]. The goal is to gain a better understanding of how the addition of tackifiers of different chemical nature can interact with the different polymeric fractions thereby changing the chemical and mechanical properties of the blend.

2. Materials and method

2.1 Components and preparation of blends

Four copolymers (2 EVAc and 2 EBA) and six tackifiers (listed along with the chemical composition and suppliers in table 1 and 2) were chosen as components for a total of twenty-four binary mixtures. Among the tackifiers, Laropal® A81 (BASF) and Regalrez™ 1094 (Eastman Chemical Company) are well known by conservators. In their pure form are used as varnishes, and have already been studied relating to their chemical stability [28-32], while rosin esters showed already a good miscibility in EVAc blends [19-21,24,25]. On the other hand, Elvax® 150 and Laropal® K80 have been selected because among the ingredients of BEVA®371O.F., thus are considered as potential references, although in binary formulations so that the copolymer – tackifier relationship could be directly studied. The ratio between tackifier and copolymer was chosen based on the ratio between tackfiers and the two EVAc in BEVA®371 (Berger's known recipe), which is equal to 1:2.5. After being weighed, the two components were put in a vial and mixed together with 60% w/w xylene (Sigma-Aldrich, >98.5% xylene mixture of isomers) under agitation at 50°C for 1h, being sure that none of the components undergo temperature-related chemical degradation at this temperature or below.

Product name & abbreviation	**Chemical nature** (a)	**Glass transition temperature [°C]** (b)	**Melting temperature [°C]**		**Melt index [g/10min]** (a)	**Onset degradation temperature[°C]** (c)	**Supplier**
			(a)	(b)			
Elvax® 150 (E)	EVAc, VAc 32%	-29	63	68	43	288	DuPont™, Wilmington, United States
Evatane® 42-60 (42E)	EVAc, VAc >41%	-29	52	56	65-85	280	Arkema,Colombes Cedex, France
Lotryl® 35BA320 (32L)	EBA, BA 32-37%	-53	66	65	260-350	330	Arkema, Colombes Cedex, France
Lotryl® 35BA40 (40L)	EBA, BA 32-37%	-52	66	65	35-45	340	Arkema, Colombes Cedex, France

Table 1: list of the chosen copolymers

(a): from products datasheet; (b): DSC analyses, same analytical method as later described; (c) TGA analysis in nitrogen atmosphere, from room temperature up to 600°C, 10°C/min

Product name & abbreviation	**Chemical nature** (a)	**Glass transition temperature [°C]** (b)	**Melting temperature [°C]** (b)	**Onset degradation temperature[°C]** (c)	**Supplier**
Laropal® K80 (K) *	Ketone resin	48	Amorphous	120	BASF, Ludwigshafen, Germany
Laropal® A81 (A)	Urea-aldehyde resin	49	Amorphous	170	BASF Ludwigshafen, Germany
Regalrez™ 1094 (94R)	Hydrogenated hydrocarbon resin	33	Amorphous	167	Eastman Chemical, Capelle aan den Ijssel, The Netherlands
Eastotac™ H-100W (EH)	Hydrogenated hydrocarbon resin	46	Amorphous	155	Eastman Chemical, Capelle aan den Ijssel, The Netherlands
Foral™ 85E (8F)	Ester of hydrogenated rosin resin	37	Amorphous	150	Eastman Chemical, Capelle aan den Ijssel, The Netherlands
Foralyn™ 5020-F CG (5F)	Methyl ester of hydrogenated rosin resin	-29	Amorphous	123	Eastman Chemical, Capelle aan den Ijssel, The Netherlands

Table 2: list of the chosen tackifiers * Discontinued product
(a): from the product datasheet; (b): DSC analyses, same analytical method as later described; (c) TGA analysis in nitrogen atmosphere, from room temperature up to 600°C, 10°C/min

2.2Differential Scanning Calorimetry (DSC)

DSC analyses were carried out in order to evaluate the miscibility between the two components through the establishment of the glass transition (T_g) and melting (T_m) temperatures. A DSC Q200 instrument supplied by TA Instruments (New Castle, United States) was used. Blends have been cast and allowed to dry for a month at ambient laboratory condition. Aluminum pans were used for housing 11mg ca of sample and the analysis followed a three-step method: heating to 120°C, isotherm for five minutes, cooling to -70°C, isotherm for five minutes, and heating again to 120°C, always at a rate of 10°C/min in a

nitrogen atmosphere. The T_gs and T_ms have been evaluated on the second heating curve, along with the enthalpy related to the melting process, which gives an estimation of the system degree of crystallinity. T_g and T_m are definable observing the second heat flow curve. T_g can be observed as a saddle point whereas the melting temperature is taken as the maximum of the endothermic peak, since the process is known to be endothermic. Enthalpy is easily calculated by the integral of the melting peak. For all these operations, Universal Analysis 2000 software by TA instruments was used.

2.3 Attenuated Total Reflection - Fourier Transform Infrared spectroscopy (ATR-FTIR)

ATR spectra have been recorded with a Smart Endurance ATR accessory with a diamond contact crystal and a ZnSe focusing element. The range investigated was from 4000 to 400 cm^{-1}, with a resolution of 4 cm^{-1}. Each spectrum is the result of the average of 64 scans. The device was inserted on a Thermo Nicolet Nexus FTIR spectrometer coupled with a DTGS detector (Thermo Scientific brand, United States). The analyses were carried out on films cast on aluminum sheets. These analyses were helpful to understand whether there was the formation of new chemical species due to the interaction between the components, as well as highlighting possible solvent retention (>5% w/w).

2.4 Rheological analyses

Blends have been characterized with a Discovery HR-1 hybrid rheometer by TA instruments (New Castle, United States). The analyses were carried out in a controlled strain (2%) mode with a cooling down ramp temperature (120°C down to 20°C) and a fixed frequency of 1Hz (comparable to an application by brush or a peel force between two canvases adhered together). The gap was maintained at 350 µm. The adhesive was applied on the heated plate as a solution, and left to dry for one hour in order to let the solvent evaporate. In order to guarantee the complete evaporation of the xylene, the analysis was repeated three consecutive times on the same specimen. At the end of the test, storage (G') and loss

(G") moduli curves were obtained and were useful to understand the stiffness of the adhesive upon activation and to find the activation temperature which is considered to be the temperature where the crossover of the curves occurs, or rather, when the product starts to become more viscous and rigid and it is no longer possible to deform it under pressure.

Another part of the curve which is considered, besides the final moduli values, is the region where the storage modulus value drops down which is also the temperature range where crystallization of the polymeric chains can occur. The wider this region, the longer the crystallization process is.

In the characterization of pressure sensitive adhesives (PSA), to verify tack properties performing rheological tests, the Dahlquist criterion is applied [33]. According to this criterion, tack occurs only when the value of the adhesive storage modulus is 50-3•10^5 Pa at the application temperature (usually room temperature) [34].

Considering the experimental blends, although the activation and tack properties are developed at higher temperatures compared to PSA, they need some pressure to be reached and for this reason the Dahlquist criterion has been taken in consideration also in this context.

2.5 Lap shear tests

Lap shear tests were done according to the ASTM standard test D-1002-10 using a Zwick 20 kN tensile tester (Zwick International, Ulm, Germany). The aim of this test is to determine the apparent shear strength of adhesives. Specimens were made with wooden slats (11x2.5x0.3 cm) cut from laminated panels. The bonded area was of 2.5x2.5 cm, sanded with 80 grit sand paper on both sides. Blends have been applied only on one of the substrates, heated to 70°C (until melted) and covered with the second slat. Samples were clamped with uniform pressure applying an office black clamp to the test area of the joint. Tests were carried out 1, 2 and 3 weeks after the application in order to evaluate the development

of the bond during the evaporation of the remained solvent. Eight specimens for each series were considered for statistical analysis.

Load speed was set at 1.3mm/min and the test ended once the load dropped to 20% of the maximum recorded load during the test. For each specimen, the maximum load, the slope of the curve and the nature of the failure were recorded.

3. Results

3.1 DSC

Theoretical values for the T_gs of the blends were calculated before doing the analyses through the Fox equation (1) [34,35]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \qquad (1)$$

This is a "user-friendly" tool to predict the T_g of the blend which in homogeneous mixtures depends on the relative amount of each component and of respective T_g although it is a simplified version of the most complex thermodynamic equation.

Tackifiers were often able to modify the polymer characteristic transition temperatures. A change only in the T_g or in the T_m of the base-polymer is the evidence of an interaction between the tackifing resins and one of the monomers of the commercial copolymer employed. In some cases, curves showed the presence of two T_gs, in between the values of the pure products, indicating different degrees of miscibility [Fig. 1 a and b].

As expected, the interaction between each single tackifier and polymer was the same for both EVAc copolymers. This behavior was similar for the tackifier/EBA blends. Laropal® K80 and Foral™ 85E have both increased the T_g of EVAc, and Laropal® K80 showed a second T_g around 10°C. The other tackifiers, on the other hand, acted as plasticizers, lowering the copolymers T_g, or they did not modify it at all [Table 3]. Moreover, among the Evatane® 42-60 blends, two other samples showed a second T_g, made with Laropal ®A81 and Regalrez™ 1094.

Both EBA blends made with the urea-aldehyde resin (Laropal® A81) have approximately the same T_g as the polymeric fraction, while all the other mixture showed an increased T_g (ΔT: +5 to +15°C). A second T_g is also obtained in blends with Laropal® K80 and Foral™ 85E.

The degree of crystallinity in the systems is investigated, taking in consideration the enthalpy of the melting process [Table 4]. In general, the presence of a small molecule does not allow the same ordered organization which is typical of the commercial polymer beads, as described also by Park et al.[Park 2006]. The solvent plays a role in this property, according to its evaporation and diffusion rate. DSC analysis of the two EVAc copolymers revealed a significantly different degree of crystallinity between them. Elvax®150 showed a high enthalpy of melting, while the high amount of VAc monomer in Evatane® 42-60 justifies the weak signal due to the melting of the crystalline fraction in the film. Comparison of the pure copolymers data with those obtained from the blends, it was observed that Eastotac™ H-100W systems showed a higher enthalpy of melting. In the blend of Elvax® 150 and Laropal® K80, the degree of crystallinity in the film appeared to be greater than in the pure polymer (normalizing to the EVAc concentration).

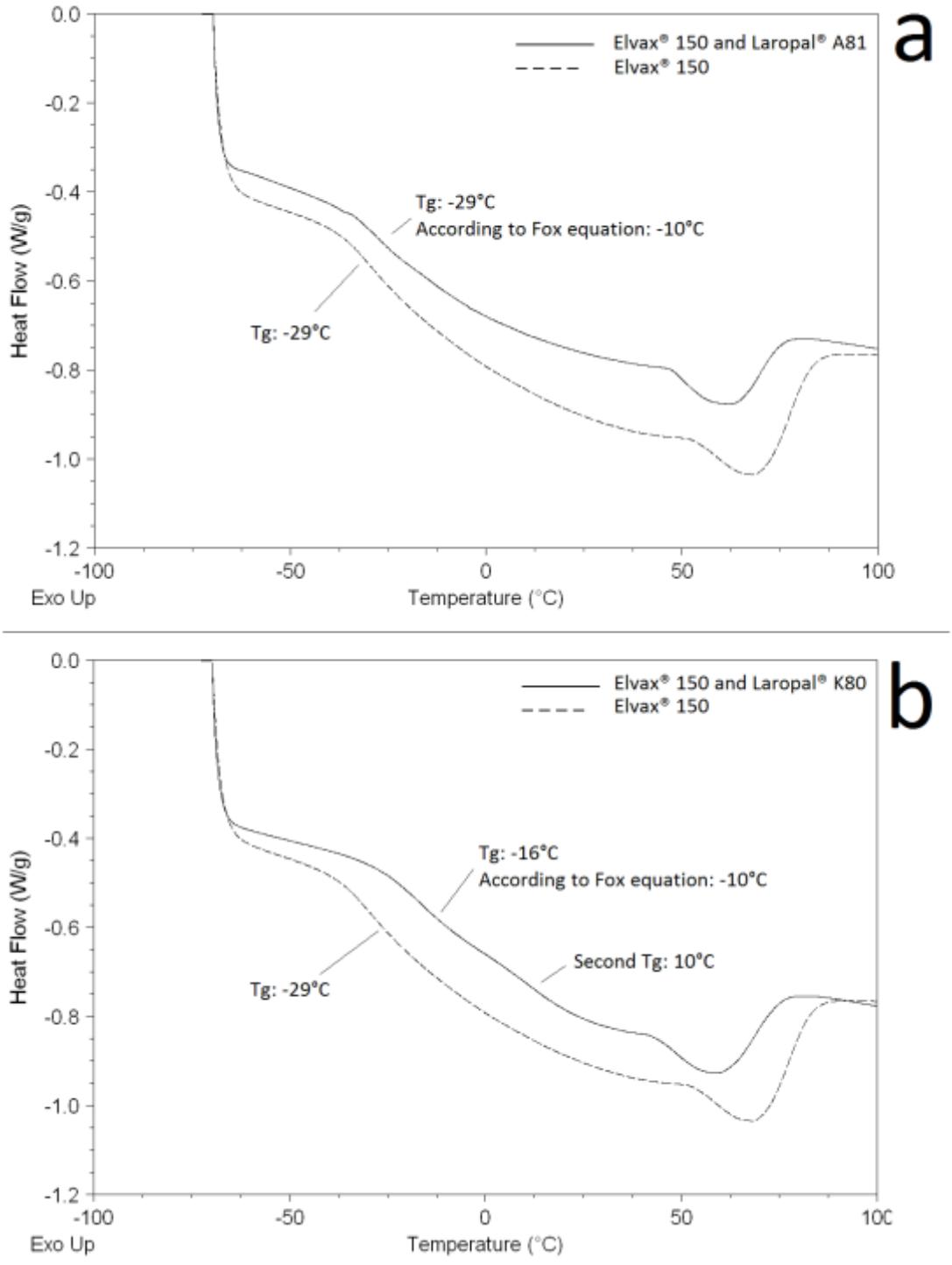

Figure 1: a) DSC curve of the blend Elvax 150 and Laropal A81 along with DSC curve of Elvax 150. T_g are reported; b) DSC data of the blend Elvax 150 and Laropal K80 compared with the curve of the pure copolymer. One of the experimental T_g of the blend is similar to the theoretical one, calculated through the Fox equation; there is also a second T_g at higher temperature.

	Glass transition temperature [°C]							
	Elvax® 150 [-29°C]		Evatane® 42-60 [-29°C]		Lotryl® 35BA40 [-52°C]		Lotryl® 35BA320 [-53°C]	
	DSC	Fox	DSC	Fox	DSC	Fox	DSC	Fox
Laropal® K80 [48°C]	-16/10	-10	-18/13	-10	-34/-5	-29	-35/-5	-30
Laropal® A81 [49°C]	-29	-9	-26/-6	-9	-50	-29	-50	-30
Regalrez™ 1094 [33°C]	-35	-13	-29/-13	-13	-45	-32	-46	-32
Eastotac™ H100-W [46°C]	-31	-10	-29	-10	-44	-30	-44	-30
Foral™ 85E [37°C]	-22	-12	-21	-12	-36/-10	-31	-33/-8	-32
Foralyn™ 5020-F GC [-29°C]	-38	-29	-35/-12	-29	-35	-46	-46	-46

Table 3: glass transition temperatures of the experimental blends along with theoretical values calculated from the Fox equation; in square brackets the glass transition temperature of the pure components

	Enthalpy of melting [J/g]			
	Elvax® 150 [9.313]	Evatane® 42-60	Lotryl® 35BA40 [8.531]	Lotryl® 35BA320 [5.3018.531]
Laropal® K80	7.57	too weak	4.60	4.66
Laropal® A81	5.82	too weak	4.18	4.46
Regalrez™ 1094	7.62	too weak	5.99	5.56
Eastotac™ H100-W	8.40	too weak	5.09	6.93
Foral™ 85E	6.86	too weak	4.40	6.79
Foralyn™ 5020-F GC	6.20	too weak	3.88	5.42

Table 4: melting enthalpy data from DSC analyses; in square brackets the enthalpy of melting of the pure copolymer

3.2 ATR-FTIR

The comparison of the spectra of the blends with those of the pure components showed there are no immediate chemical changes occurring upon mixtures and the samples are only physical mixtures whose state arises from different interactions between functional groups and other factors like steric hindrance, etc... Furthermore, after a month, there were no peaks ascribable to xylene residues (peaks at 1516, 767 and 742 cm^{-1}).

3.3 Rheological analyses

The storage modulus curves (G') of the mixtures at room temperature (20°C) is often lower than that for the individual components, an indication that the tackifier acts as a plasticizer. Crossover points were shifted towards lower temperatures [Table 5] and, in general, the curve is close to that of the copolymer, as expected since it is the major ingredient. The Dahlquist criterion was always satisfied.

Among the Elvax® 150-based blends, those made with Laropal® K80 and Foral™ 85E showed similar behaviours, and the most significant difference was in the crossover temperature [Fig.2].

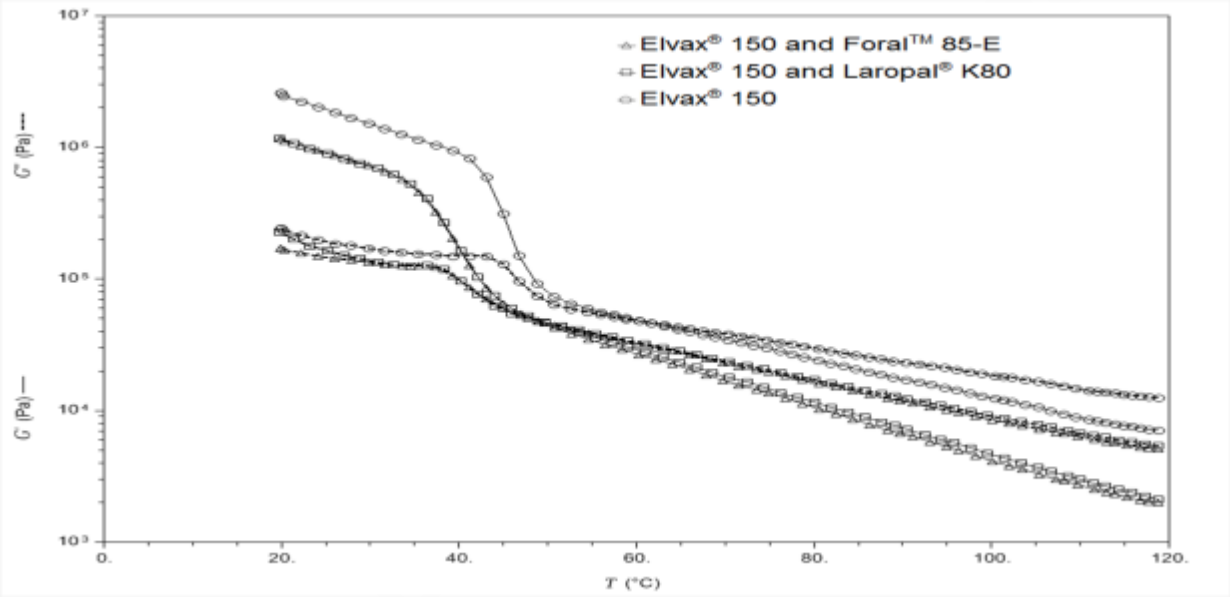

Figure 2: storage (G') and loss (G") moduli of Elvax 150 with Laropal K80 (dark grey) and Foral 85E (black) blends along with the pure copolymer curves (light grey); the rheological test underlined the similar behaviour of the two mixtures and one of the main differences is the temperature at which the crossover occurs

Although formulations with the hydrogenated hydrocarbon resin Eastotac™ H-100W showed a higher degree of crystallinity, they were not the most rigid; furthermore, among them, EBA blends with this tackifier showed the lowest crossover temperatures. In Lotryl® 35BA40 systems, Laropal® K80 and Regalrez™ 1094 and the two rosin esters (Foral™ 85E and Foralyn™ 5020-F CG) as well revealed to have

similar rheological properties. The mixture of this copolymer with Eastotac™ H-100W was significantly different, with a G' modulus value of 105 instead of the 106, as measured for the other blends [Fig.3].

	Crossover points (temperature vs G'=G" moduli)							
	Elvax® 150 [61°C, 47.597 Pa]		Evatane® 42-60 [47°C, 107.274 Pa]		Lotryl® 35BA40 [70°C, 29.971]		Lotryl® 35BA320 [53°C, 41934 Pa]	
	[°C]	Pa	[°C]	Pa	[°C]	Pa	[°C]	Pa
Laropal® K80	51	45288	50	79363	57	32676	48	42673
Laropal® A81	52	65261	29	48732	51	10753	51	44369
Regalrez™ 1094	41	52274	44	155808	51	30207	40	13683
Eastotac™ H100-W	46	56467	45	126532	41	2664	40	42190
Foral™ 85E	48	50353	46	66086	52	26467	44	35284
Foralyn™ 5020-FGC	41	44988	31	77407	49	23534	42	22836

Table 5: coordinate of the crossover points of the blends in rheological tests along with those of the pure copolymers (temperature vs G'=G" moduli)

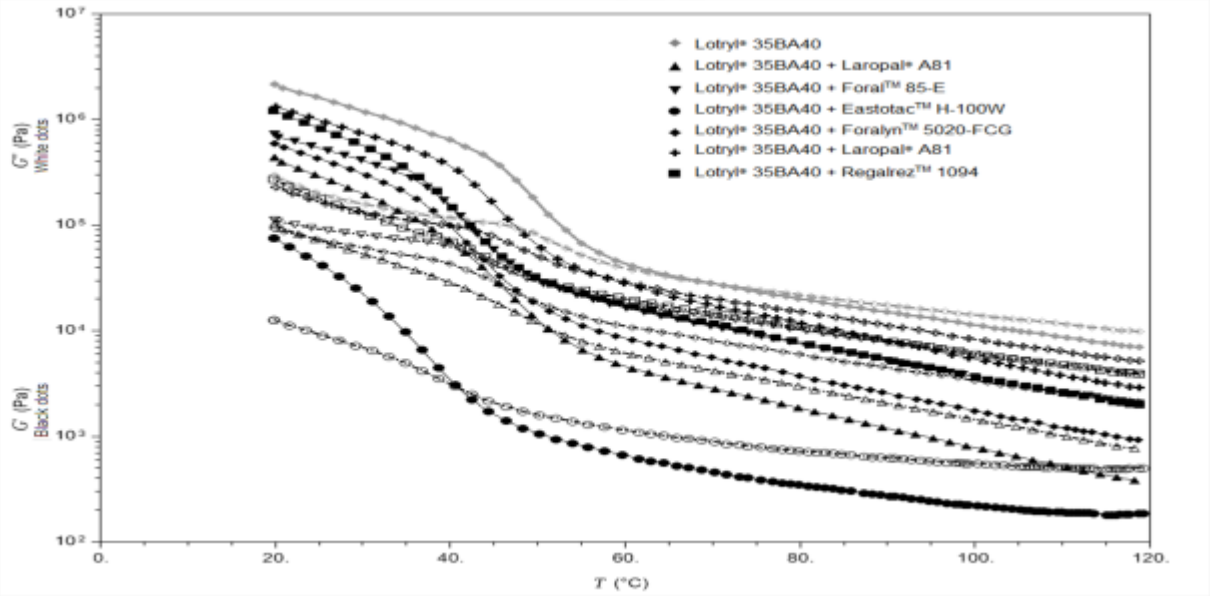

Figure 3:
rheological curves of the Lotryl® 35BA40- based blends along with the pure copolymer. The blend made with this EBA copolymer and Eastotac™ H-100W showed a significant different and increased behaviour from the other mixtures

A comparison among all the EBA formulations showed that the major difference is the crossover temperature which is around 53°C for Lotryl® 35BA40 (higher molecular weight) and around 45°C for Lotryl® 35BA320. The values of the final G' modulus is approximately the same in all cases.

3.4 Lap shear tests

Lap shear results as a function of retention time at laboratory condition before testing are presented in fig. 4. Among all the formulations, those made with Elvax® 150 showed the highest lap shear values. All the other values can be considered comparable in the final results, within the standard deviation, although Lotryl® 35BA40 blends have slightly higher values, especially for blends made with Eastotac™ H-100W.

There is not a general tendency correlating evaporation of the solvent with the measured mechanical properties. Nevertheless, EVAc copolymers showed decreasing shear strenght values with time; on the contrary, both the EBA copolymers showed an increase in the maximum shear force registered after two weeks and a stabilization (Lotryl® 35BA320) or a low decrease after three weeks.

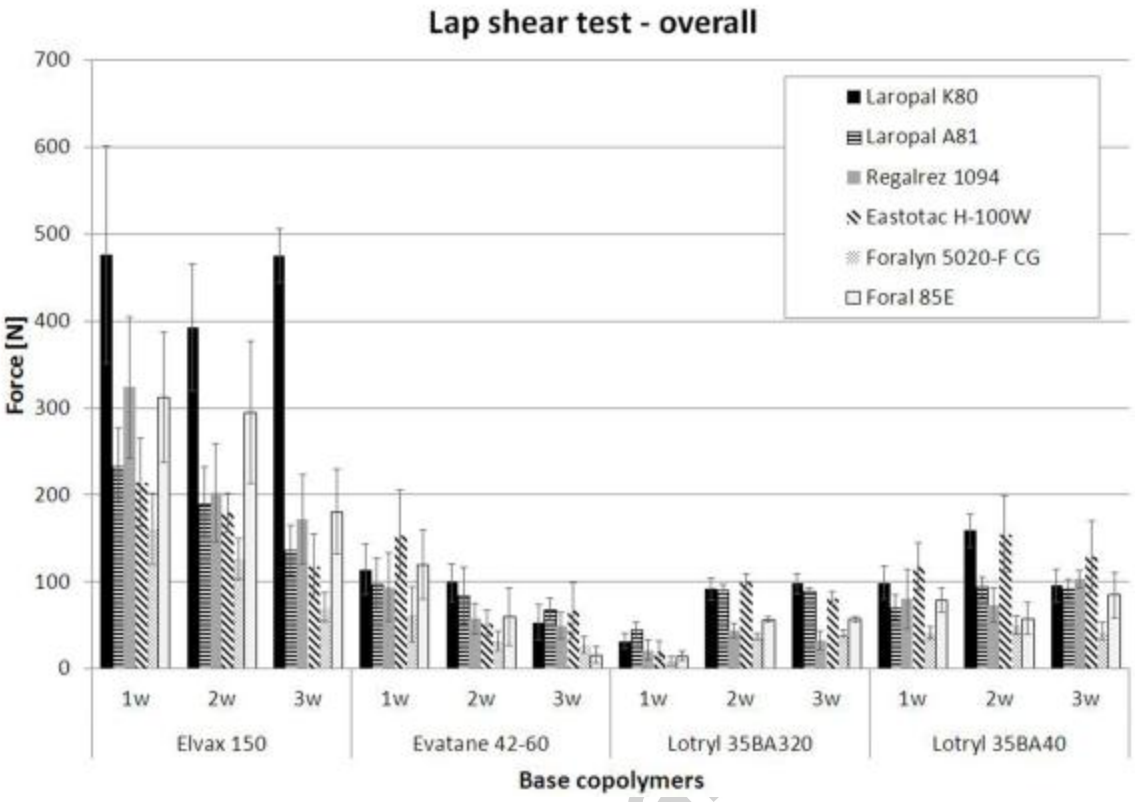

Figure 4: lap shear test results plotted according to the base copolymers and the waited time before testing (1w= 1 week, 2w= 2 weeks, 3w= 3 weeks)

In order to investigate the relative elasticity of the blends, curves of the lap shear test were compared (Fig. 5 a and b). EVAc blends curves have stiffer slopes than EBA curves, suggesting that the butyl acrylate comonomer gives elastic properties to the copolymer. All the formulation showed to have good elongation characteristics and this was confirmed also by the type of failure which always occurred. All the binary mixtures failed 100% cohesively inside the adhesive layer, and often the two wooden substrates have not fallen apart during the test, evidence of an elastic recovery since the pulled slat was able to return in the initial position.

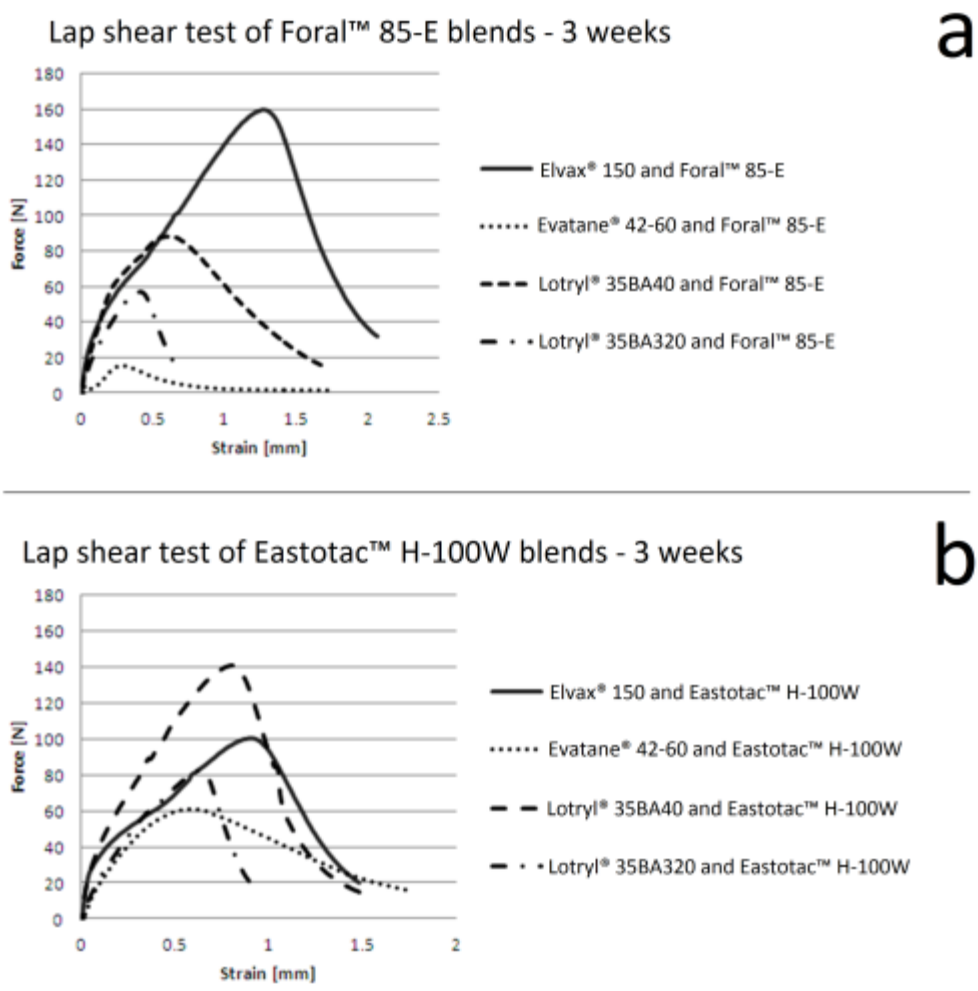

Figure 5: lap shear curves obtained testing specimens after three weeks from the application of the adhesives. **a)** Foral 85E blends and **b)** Eastotac H-100W blends. *: in this case the wooden slats fell apart

4. Discussion

In general, it was possible to observe similar behaviours within the two groups of blends (i.e. EVAc and EBA binary mixtures). The interpretation of the DSC blends curves was aided by the Fox equation; the experimental values were reasonably similar to the theoretical one only in few blends, the latter indicating a partial miscibility or structural ordering between the components. In some cases, cast films

showed a separation of phases, recognized because of the opacity; this is likely due to a non miscibility of the components at room temperature, after the evaporation of the solvent.

EVAc copolymers were more influenced by ketone resins and by one of the rosinate resins (Foral™ 85E). In particular both the rosin ester resins lowered the melting temperature, an indication of an interruption of the resin with the polyethylene crystalline fractions. In the Elvax® 150 DSC curves it was always possible to recognize the maximum point of the crystal melting transition, while with the Evatane® 42-60 the melting peak is weak and broad.

DSC analysis of the EBA blends did not show substantial changes in the T_m of the copolymers. Laropal® K80 and rosinate resins (Foral™ 85E and Foralyn™ 5020-F CG) increased the T_g by at least 10°C, due to interaction with the butyl acrylate groups. Furthermore, with the same tackifiers, it was possible to observe a second T_g. All these blends show a well defined melting peak due to the polyethylene crystalline domains.

The increase of the second T_g could suggest the appearance of different phases in the solid state, i.e. a preferential interaction between the tackifier and one of the monomers of the polymer, or a possible miscibility between the two ingredients, but in a different concentration than the one studied. This phenomenon has already been described by Barrueso-Martinez et al. [25], although in mixtures of different chemical nature (EVAc with 32-34% of VAc + polyterpene resin, unspecified ratio). To be underlined, the fact that Laropal® A81 and Regalrez™ 1098 only when added to Evatane® 42-60 (i.e. the EVAc with the higher VAc amount) showed two T_g revealing a preferential interaction of these two resins with the VAc groups.

In these cases where no change in the T_g of the copolymer was observed, it was expected to see the T_g of pure tackifiers. However, in all cases this was not detected, but it must be considered that, due to the lower concentration, most likely the signal is hidden by the melting peak of the copolymer, which begins around the same temperature.

From the mechanical tests, it was not possible to determine if these domains in the mixture can affect the tack properties and the mechanical handling behaviour of the adhesive once applied or at the activation temperature.

All the blends showed a crossover point, so these mixtures can be suitable as HSA. The crossover point occurred in a range of temperatures between 41°C and 57°C. Since it is possible to consider this point as the "activation temperature" of the adhesive, these mixtures can be considered, in general, safer than BEVA®371 for the works of art since they do not need to be heated up to as high a temperature in order to develop tack properties. It is also an advantage when among the artist materials there are (semi)crystalline materials with a relatively low melting temperature, e.g. wax or grease, which would be damaged by the application of HSA with activation temperature higher than their melting point. Furthermore, also low T_g materials, such as acrylics, cannot effort heating since they can be deformed if above their glass transition temperature or close to their softening point.

The addition of a tackifier to a copolymer leads to changes in chemical and mechanical properties as compared to the pure copolymer. Due to the presence of another molecule, the system cannot reach the same level of order in the solid state, which means that in semi-crystalline copolymers, the percentage of crystallinity is reduced whenever another component is added. As seen in rheological results, the mechanical properties of the blends at room temperature were in general lower than those of the base-polymer themselves, because of the decreased storage modulus value at 20°C.

From this analysis, the difference in molecular weight of the EBA copolymers has been underlined only by the crossover point which has occurred at lower temperatures for Lotryl® 35BA320. From a mechanical point of view, its blends revealed to be weaker, which is consistent with data reported by Park et al. [23] about the relationship between melt index and lap shear strength.

As mentioned before, the amount of VAc in Elvax®150 is comparable with the amount of BA in the two Lotryl® copolymers. The polymerization with these two comonomers leads to different mechanical

properties in the final product. In fact, lap shear and rheological tests showed that blends made with Elvax®150 at room temperature (20°C) have greater storage modulus values and lap shear strength. On the other hand, EBA blends revealed to be more elastic, although weaker.

The mechanical analyses of specimens let dry for 1, 2 and 3 weeks after the application of the adhesive did not give any significant information about the development of tack and resistance properties. The plot of the lap shear results did not highlighted any specific trend related to the solvent evaporation or retention from and in the adhesive layer. Nevertheless, in EVAc blends it was seen a decrease of lap shear strength during time, while in EBA blends a weak improvement of the mechanical properties followed an initial decrease of them. This can be ascribed to a different entanglement of the bulk structure of the adhesive film.

The high standard deviation observed in the lap shear results can be due to the application method which is sensitive to perception of the worker, but it is most likely due to the wooden substrate and its physical characteristic (porosity, fibers, etc.).

5. Conclusions and further developments

EVAc and EBA copolymers seem to be the most suitable products for HSA adhesives for conservation purposes due to characteristic temperatures values within harmless condition for works of art and the capacity to be modeled under low pressure. Moreover, they can be blended with other ingredients so that their softening point and tack development can be shifted to lower temperatures, which helps reducing thermal damage to the art object.

As the analyses showed, rosin esters and the ketone resin have acted as tackifiers since they were able to increase the glass transition temperature of the copolymers. They revealed to be miscible with the

polymeric components, although not always completely in the ratio investigated, as suggested by the second Tg in their DSC curves. Rheological analyses showed similar behaviours for these mixtures. The urea-aldehyde resin together with the two hydrogenated hydrocarbon resins did not show a good miscibility with EVAc and EBA copolymers. Although DSC data underlined they had almost no effect on the glass transition and on the melting temperatures of the base copolymer, mechanical analyses (i.e. rheological and lap shear tests) highlighted that they are able to modify the properties of the final formulation. Furthermore, blends with Eastotac^{TM} H-100W showed the highest degree of cristallinity among all the experimental mixtures.

The research will continue, improving the rheological data, finding an appropriate time-temperature superposition method. Lap shear tests will be carried out on different substrates and with different application methods in order to reduce the standard deviation, but also 180° and T-peel test will be performed in order to simulate condition of application closer to real cases.

Moreover, systems will be characterized by nuclear magnetic resonance and creep ageing test. In order to investigate the range of miscibility between EVAc and EBA copolymers and tackifiers, research on blends with different ratios will be carried out, along with chemical stability through UV-light ageing.

The influence of wax will be studied as well, but in a second time once accessed the most suitable binary mixtures. For this study, UV-stabilizers have not been added to the blends, but the delicate application field requires products to be stable and reversible, thus investigations in this sense must be performed, before arriving at the trial phase with the application of the best performing mixtures on mockups. Evaporation of the solvent will be evaluated by pyrolysis-gas chromatography/mass spectroscopy, also considering that once applied the evaporation surface is really small and the boiling point of the xylene is ca 140°C, so it could remain for a long time in the adhesive film.

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