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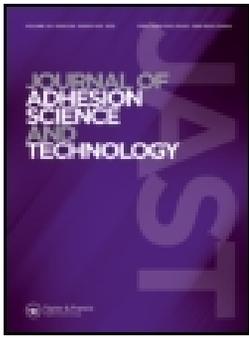
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The photostability and peel strength of ethylene butyl acrylate copolymer blends for use in conservation of cultural heritage

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ABSTRACT

Materials, both natural and synthetic, are used as adhesives or consolidants during the conservation of cultural objects. However, few adhesives have been formulated specifically for the needs of cultural heritage. This article describes a study of the stability of ethylene butyl acrylate copolymers as well as blends of these polymers with low molecular weight resins, which may be used as consolidating adhesives for flaking and fragile paint layers. The materials were aged under simulated museum conditions. Fourier-transform infrared spectroscopy and size exclusion chromatography were used to analyze changes in chemical structure and molecular weight distribution, respectively. The degree of degradation was found to be dependent on the specific blend composition. With the addition of a hindered amine light stabilizer, minimal changes occurred in the molecular weight distribution and no loss in polymer solubility were noted. Therefore, it is suggested to incorporate a stabilizer into ethylene butyl acrylate polymer blends to extend their life and safe use in cultural heritage. Differential scanning calorimetry was employed to investigate the miscibility of the binary blends and the temperature window of their application. Furthermore, adhesive peel strength for the individual components and the binary mixtures revealed values comparable to that of ParaloidTM B-72, a frequently used consolidant. Consolidation tests on the blends were done by professional conservators on mock up and dummy paintings.

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Photochemical stability; conservation; EBA; ethylene butyl acrylate copolymer; low molecular weight resin; hindered amine light stabilizer; adhesion; T-peel strength; viscosity

1. Introduction

Paintings have a complex structure as they are composed of multiple layers of varying materials. These typically include a textile, wood or other support layer, a glue size layer,

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a ground layer, several paint layers and often a varnish layer. In many cases, the chemical and mechanical properties of these materials are mismatched [1–3]. Changes in environmental conditions including temperature and relative humidity may cause the components to react differently [4]. Consequently, stresses introduced within the painting as well as chemical changes may result in cracking or flaking of the paint layers.

To conserve such paintings, conservators have turned towards consolidating adhesives to re-adhere fragile and flaking material. Naturally occurring adhesives, such as animal glues, waxes and gums, have been used but may degrade over time [5,6]. This can result in discoloration of the consolidant and/or bond failure. Even worse, the consolidant might become insoluble in ‘safe’ solvents, which makes further restoration difficult [7]. In the twentieth century, synthetic materials have been introduced to address these shortcomings [7]. Most of these adhesives have been formulated for industrial purposes, with only a few products formulated and tested specifically for the conservation field. But these products might lack the optimal chemical, mechanical durability properties required for the demanding restorative tasks [6,7]. Therefore, it is vital to develop and test new materials before their use as consolidating adhesives.

There are several factors that must be considered when choosing a consolidating adhesive [3,7,8]. Although strict reversibility, that is the ability to remove the material at a later stage, may be difficult or impossible for consolidants [7], chemical and physical stability as well as preservation of solubility are important. Chemical changes to the consolidating adhesive upon aging, such as oxidation or cross-linking, may leave the material insoluble.

These high demands limit the types of adhesives suitable for conservation based on their chemistries. Consequently, thermoplastic adhesives have been introduced to the field for their ability to be heated and cooled many times without cross-linking or forming irreversible bonds, both cohesively and adhesively. Specifically, copolymers, of acrylates, methacrylates, vinyl alcohols, vinyl acetates, and ethylene have been used as consolidating adhesives, all of which show varying degrees of stability [7,9,10].

A popular synthetic adhesive that has been formulated for conservators is BEVA[®] 371 [11–13]. This multicomponent system can be used as a hot-melt and heat-seal adhesive, typically delivered in a solvent and contains several components including two poly(ethylene-*co*-vinyl acetates) (EVAs), two low molecular weight (LMW) resins, and a wax. Initially introduced for canvas relining, BEVA[®] 371 has been adapted by conservators for use as a general consolidating adhesive. The main component, EVA, has been thoroughly investigated for its photostability (Figure 1(a)) [14]. Under simulated museum conditions, studies show negligible degradation with minor cross-linking and chain scission of the EVA copolymer. Consequently, these polymers have been considered relatively safe for use in conservation.

More recently, adhesives based on poly(ethylene-*co*-butyl acrylate) (EBA) have been investigated as alternatives for traditional EVA hot-melt adhesives (Figure 1(b)). EBAs show a wider solubility range than EVAs and could therefore be more attractive for conservation purposes [15–19]. However, their photostability under museum conditions has yet to be reported and should be investigated before a recommendation can be made.

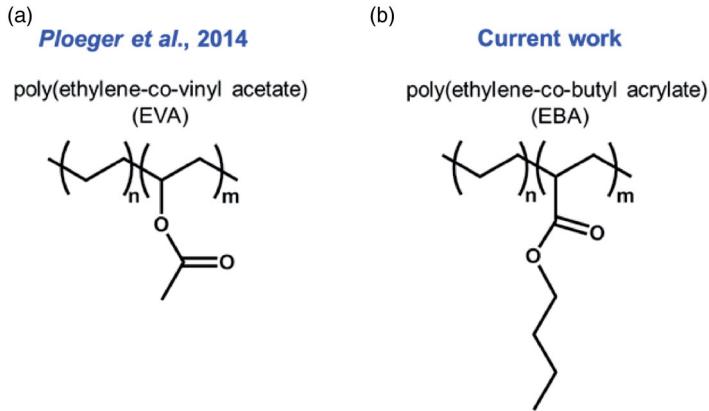


Figure 1. Chemical structures of poly(ethylene-co-vinyl acetate) [14] and poly(ethylene-co-butyl acrylate) [15].

Low molecular weight resins

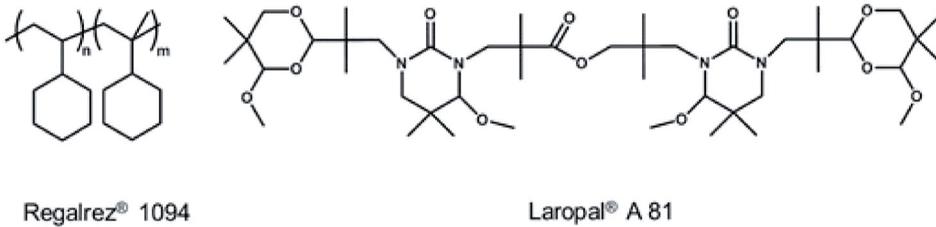


Figure 2. Chemical structure of low molecular weight resins Regalrez® 1094 [7] and the proposed structure of Laropal® A 81 [7].

Hot-melt adhesives are typically formulated with the addition of a low molecular weight resin [20,21]. These resins tune the working properties of the adhesive by reducing its viscosity and increasing the hot tack to assist in the assembly of the final product [11,20,22]. In addition to affecting adhesive tack, peel strength may also increase with addition of low molecular weight resins to the adhesive formulation [23]. Photostability studies have been reported for low molecular weight resins Laropal® A 81 [8,24,25] and Regalrez® 1094 [8,18,26], materials commonly used in cultural heritage (Figure 2). Laropal® A 81 (BASF) is a urea-aldehyde resin while Regalrez® 1094 (Eastman) is a hydrogenated hydrocarbon resin. These low molecular weight resins are relatively stable and are therefore good candidates for use in adhesive blends.

For this study, EBA copolymers Lotryl® 35BA320 and Lotryl® 35BA40 (Arkema) were investigated for their photostability under museum conditions by accelerated light aging. These ethylene butyl acrylate copolymers have identical co-monomer ratios but differ in their molecular weights. The EBA copolymers have an ethylene content of ~63–67% and butyl acrylate content of ~33–37% by weight, where Lotryl® 35BA320 is lower in molecular weight than Lotryl® 35BA40 [27,28].

The EBA copolymers were blended with low molecular weight resins Laropal[®] A 81 or Regalrez[®] 1094 (Figure 2). Additionally, a hindered amine light stabilizer (HALS), Tinuvin[®] 292, was added to each of the four polymer blends in an effort to inhibit photodegradation [8,29]. HALS are known to inhibit degradation of various polymers [30–32] and have already proven to be effective in preservation of cultural heritage materials [8,14]. The viscosity and the T-peel strength of the lower molecular weight copolymer Lotryl[®] 35BA320 blended with low molecular weight resins were measured to determine the adhesive properties on flaking paint layers. Chemical and physical changes were observed using size exclusion chromatography (SEC), Fourier-transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC). The surface energy of an alkyd paint that was used as a test substrate was measured to understand the wetting by the adhesive blends.

2. Materials and methods

2.1. Materials

Lotryl[®] 35BA320 and Lotryl[®] 35BA40 were obtained from Arkema (Colombes, France). Laropal[®] A 81 and Regalrez[®] 1094 were obtained from CTS Europe (Portsmouth, UK). Tinuvin[®] 292 was purchased from Kremer Pigmente GmbH & Co. (Aichstetten, Germany). Reagent grade toluene and analytical grade tetrahydrofuran (THF) were purchased from VWR (Radnor, PA). Standard pre-ground canvas (Rijn Uni) was purchased from Claessens Canvas (Waregem, Belgium) and Winsor & Newton Griffin Alkyd Oil Paint Lemon Yellow series 1914722 pigment PY3 was obtained from Winsor & Newton (London, UK).

2.2. Adhesive blend preparation

Blends of Lotryl[®] 35BA320 or 35BA40 and Laropal[®] A 81 or Regalrez[®] 1094 were prepared in toluene. Copolymers and low molecular weight resins were combined in two ratios, a 1:5 (for mockup tests only) and a 1:1 ratio (for mockup as well as physical and chemical tests) by dry weight of copolymer to dry weight of low molecular weight resin (weight/weight). Solutions of the 1:1 ratio were prepared at 20% of solid dry weight of base polymer + low molecular weight resin per weight of solvent (weight/weight).

2.3. Film preparation for accelerated aging

The procedure for film preparation was reported previously [8]. Standard microscope slides (75 mm × 25 mm) were cleaned with acetone followed by ethanol and dried with compressed air. Adhesive blends were prepared at 20% (weight/weight) in toluene and were heated at 50 °C. A 0.8 mL of this solution was dispensed onto these slides and allowed to spread across to form a film (thickness: approximately 0.25 mm on average). Films were dried for 4 weeks under ambient conditions to allow the solvent to evaporate. Eventually, HALS Tinuvin[®] 292 was added to the polymer blends at 2% (weight/weight) to study the effect of inhibition of photodegradation.

2.4. Accelerated aging

The accelerated aging conditions of museum illumination [26] have been reported previously [8]. Experimental conditions were modified from ASTM D4459, using an Atlas Xenotest Alpha High Energy weathering instrument equipped with a Xenon arc (an irradiance of 42 W/m^2). Indoor conditions [33] mimicking daylight passing through window glass were simulated, at 40°C and 40% RH. A Xenochrome 320 glass filter was used to block UV radiation below 320 nm. All films were aged for a maximum of 6 weeks, which is equivalent to 1008 h.

2.5. Determination of gel content

The amount gelation of the blends, before and after aging, gave information about the change in solubility, and, thus, its stability. Gel content of films was determined gravimetrically after 6 weeks of irradiation following a modified procedure [34]. Aged films were dissolved at 1 mg/mL in THF and vigorously stirred for 24 h. The insoluble fractions were collected by vacuum filtration using Whatman filter paper, size 4–7 μm , and dried under ambient conditions until masses were stable.

2.6. Fourier-transform infrared spectroscopy (FTIR)

A Perkin Elmer Spectrum 100 Fourier-transform infrared spectrometer equipped with a universal attenuated total reflectance (ATR) sampling accessory and a ZnSe crystal was used to analyze cast films on glass slides, as reported earlier [8]. Data were collected at 16 scans with a resolution of 4 cm^{-1} . A minimum of three spectra in various film areas were measured per sample. No notable differences were observed between areas, therefore, the ATR-FTIR spectra were not normalized, and one spectrum was chosen for representation.

2.7. Size exclusion chromatography (SEC) and software

Changes in molecular weight distribution of unaged and aged polymer blend films were monitored using size exclusion chromatography (SEC), as reported previously [8]. A Shimadzu Prominence Ultra-Fast Liquid Chromatography system equipped with a Shodex GPC LF-804 column ($8.0 \times 300.0 \text{ mm}$) and a refractive index detector was used. Unaged and aged (3 and 6 weeks) films were dissolved at 1 mg/mL in unstabilized THF. Samples were run at 1 mL/min with THF as the eluent and the instrument was maintained at 40°C . Approximate molecular weights were calculated from a calibration curve using polystyrene standards. Number averages molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index ($\text{PDI} = M_w/M_n$) were calculated for all materials.

For the bimodal SEC chromatograms, Fityk software was used to deconvolute the peaks [35]. The peaks associated with either the copolymer or low molecular weight resin were fed back into the SEC software to determine the molecular weight and PDI.

2.8. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was employed to investigate the miscibility of the 1:1 (weight/weight) binary blends. These measurements provide information on the thermal transitions such as the glass transition temperature (T_g), the melting temperature (T_m), and crystallization temperature (T_c). A TA Instrument DSC 250 was utilized for the measurements. The binary blend test samples, were prepared in exactly the same way as those for the aging tests. They were cast and dried at 22 °C and 50% environmental relative humidity for one week. Subsequently, about 11 mg of each sample, was hermetically sealed using Tzero aluminum pans, while an empty pan was used as a reference. For the measurements, the samples were heated and cooled and again heated in three subsequent cycles. In the first heating cycle, the samples were heated from room temperature to 120 °C at 10 °C/min, maintained at 120 °C for 5 min and cooled from 120 °C to -100 °C at 10 °C/min, maintained for 10 min at -100 °C, and finally heated again from -100 °C to 120 °C at 10 °C/min. All the measurements were performed in triplicate. The glass transition temperature (T_g) is measured as the midpoint of the heat flow change. The melting temperature (T_m) is reported as the minimum point of the endothermic melting peak in the first heating scan. The enthalpy of melting (ΔH_m) is calculated as the area of the endothermic melting peak in the first heating scan. The crystallization temperature (T_c) is identified as the maximum point of the exothermic crystallization peak in the cooling scan.

2.9. T-Peel strength and failure type of adhesives

A procedure reported previously was followed to prepare substrates for testing [8]. Test specimens were prepared using two flexible substrates of pre-ground canvas (305 mm × 25 mm). Alkyd oil paint was applied to the canvas pre-ground surface using a precision thin film applicator of 200 μm and then dried at room temperature. Using a syringe, 1.3 mL of polymer solution at 20% (weight/weight) in toluene were applied to one of the paint substrates to cover the bonded area (241 mm × 25 mm). A 200 g weight was applied as they were dried in a vacuum oven for 1 h, and after removing the weight during 23 h, and consecutively 6 days[®] under vacuum at 100 mbar, all at 50 °C.

The peel strength of the adhesives was measured according to the ASTM standard D 1876 using a Zwick 20 kN tensile machine equipped with a 1 kN load cell. The load was applied at a constant speed of 254 mm/min. A minimum of 8 specimens were tested per adhesive type and an average value is reported.

The type and amount of failure of each tested sample was visually determined. The highest expected standard deviation in the visual observation on partial adhesive failures is expected to be at the most ±7%.

2.10. Contact angle measurements

Contact angle measurements were done to determine the surface energy of both the alkyd paint applied to the standard pre-ground canvas and the acrylic ground layer itself, performed on a CAM 200 instrument. Ten separate measurements of 5 μl drops of each

test liquid (distilled water, aniline, and ethanol and glycerol) were averaged, and the interfacial free energy γ_{SL} was obtained using the Owens and Wendt equation [36].

2.11. Viscosity

Viscosity is an important rheological characteristic at the application of adhesives, as it is the resistance of a the adhesive to flow during the bonding process [37]. The performed tests were based on ASTM D445-19a [38]. For these viscosity tests a SCHOTT glass capillary Ubbelohde kinematic viscometer was used (ref: 532 10 with capillary length $L = 70$ mm, diameter $R = 0.315$ mm, and volume of the measuring bubble: $V = 21.82$ mm³ and calibration constant: $K = 0.009606$ mm²/s²) in a temperature controlled visibility bath (controlled by a SCHOTT CT52 thermostat) at 25 °C and 60 °C.

Four different mixtures were prepared, in a ratio by dry weight of copolymer to dry weight of LMW (low molecular weight) resin (weight/weight) of: 1:0, 1:1, 1:5, and 0:1. The dynamic viscosity of the blends was measured at three different solution concentrations (0.5%, 1% and 2% weight/weight in toluene, due to instrumentation limits). Each reported data point was averaged from 5 measurements.

2.12. Consolidation tests

Two sessions of one day including one day of consolidation experiments were done to determine the suitability of the adhesive blends. This was carried out by two groups of 10 professional painting conservators.

The first day, an evaluation form to rank the properties and performance of the adhesive blends, was defined (Table S6) and used during the conservation tests on the second day. The description and photographs of the mock-up and dummy paintings can be found in the Supplementary data (Supplementary Text, Figures S8–S14).

3. Results and discussion

3.1. DSC

DSC was performed to investigate the compatibility between the components in the binary mixtures of Lotryl[®] 35BA320 with the tackifiers (Laropal[®] A81 and Regalrez[®] 1094) (1:1 weight/weight) as well as the serviceability temperature window of such mixtures. Table 1 summarizes the values for glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), and melting enthalpy (ΔH_m) for EBA copolymer, the tackifiers, and their mixtures.

Table 1. DSC results from the researched materials as well as their (1:1 w/w) mixtures.

	T_g (°C)	T_m (°C)	T_c (°C)	Melting enthalpy (J/g)	T_c range (°C)
EBA (Lotryl [®] 320)	-53 ± 0.6	64 ± 0.5	46 ± 0.2	12.5 ± 0.6	37–68
Laropal [®] A81	46.5 ± 0.2	–	–	–	–
Regalrez [®] 1094	38.5 ± 0.5	–	–	–	–
EBA-Laropal [®] A81	-53.5 ± 0.5	62.5 ± 0.5	44.5 ± 0.0	8.3 ± 0.8	35–56
EBA-Regalrez [®] 1094	-50 ± 1	55.2 ± 0.2	32.2 ± 0.2	14.8 ± 0.9	24–40

Including: T_g , the glass transition temperature; T_m , the melting temperature; T_c , the crystallization temperature during cooling.

Lotryl[®] 35BA320 can be regarded as a semi-crystalline polymer in which the polyethylene sections of the copolymer chain arrange themselves in crystalline domains. As shown in Table 1, both Laropal[®] A81 and Regalrez[®] 1094 are amorphous resins demonstrating a glass transition temperature around 46 °C and 35 °C, respectively, in agreement with what was found by Maines [39]. The existence of a T_g close to the pure copolymer suggests a non-miscibility or at least a limited miscibility between the components of the binary mixture. This is in line with the findings of Cimino et al. [18]. The reduction in T_m and T_c and the T_c range is more significant in the case of the EBA/Regalrez[®] 1094 binary mixture. It can also be observed that the presence of tackifiers interferes with the degree of crystallinity of the systems, linked to their enthalpy of melting. The overall melting enthalpy of the EBA/Regalrez[®] 1094 binary mixture seems to increase while a reduction in the melting enthalpy of EBA/Laropal[®] A81 can be observed. However, care should be taken that the binary mixture only contains 50% (by weight) of crystalline polymer. Hence, if the melting enthalpy (J/g) of the mixtures would be multiplied by two, one can calculate the melting enthalpy (hence, the amount of crystallinity) of the EBA constituent in the binary mixture. This results in a melting enthalpy of 16.6 and 29.6 J/g for the Laropal[®] A81 and Regalrez[®] 1094 system, respectively. The significant increase in the degree of crystallinity of the polyethylene domains of the EBA/Regalrez[®] 1094 mixture can be attributed to the non-polar nature of the Regalrez[®] 1094. It is hypothesized that the better compatibility between Regalrez[®] 1094 and the non-polar polyethylene section of the EBA copolymer leads to partial migration of Regalrez molecules in-between the polyethylene chains acting as plasticizer and causing increased mobility of polyethylene chains. Increased mobility of polyethylene chains can lead to more chain folding and crystallization growth in polyethylene domains. However, the remarkable reduction in melting temperature of EBA/Regalrez[®] 1094 can be due to the formation of smaller and less (perfect) crystalline polyethylene domains.

3.2. Aging

Lotryl[®] 35BA320 and Lotryl[®] 35BA40, and blends with Laropal[®] A 81 and Regalrez[®] 1094 were aged under simulated indoor conditions. The accelerated aged blends containing the higher molecular weight copolymer Lotryl[®] 35BA40 are reported in the Supplementary Data (Figures S1–S3 and Tables S1–S5).

Size exclusion chromatography was used to determine the approximate molecular weight averages of the unaged copolymers and low molecular weight resins. Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index ($PDI = M_w/M_n$) were calculated for all materials (Table 2). The average molecular weights for the low molecular weight resins Laropal[®] A 81 and Regalrez[®] 1094 fall outside the calibration range. Therefore, these values have been extrapolated from the polystyrene calibration curve.

3.3. Lotryl[®] 35BA320

Monitored by FTIR, irradiation of Lotryl[®] 35BA320 showed minimal structural changes with minor oxidation of the polymer. There is very slight increase in

Table 2. Molecular weight averages of unaged base polymers and low molecular weight resins [8, 35].

Polymer	M_n	M_w	PDI (M_w/M_n)
Lotryl [®] 35BA320	30,000	100,000	3.3
Lotryl [®] 35BA40	31,000	148,000	4.8
Laropal [®] A 81	1400	3500	2.5
Regalrez [®] 1094	800	1200	1.5

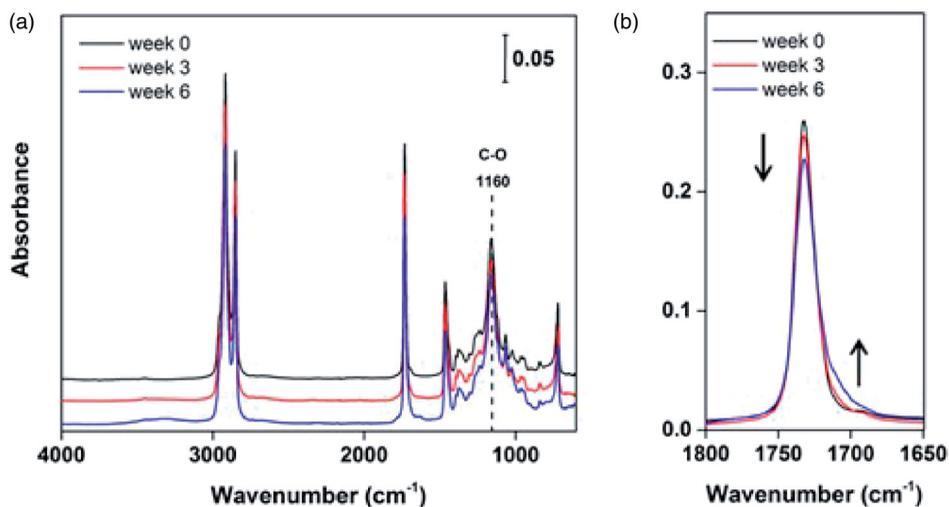


Figure 3. FTIR spectra of unaged (black), week 3 (red), and week 6 (blue) aged copolymer Lotryl[®] 35BA320. (a) Offset of FTIR spectra from 4000 to 650 cm^{-1} . Dashed line at 1160 cm^{-1} highlights the C-O absorption band. (b) FTIR spectra of the carbonyl peak at 1732 cm^{-1} .

absorption in the hydroxyl region between 3600 and 3050 cm^{-1} at week 6 of irradiation (Figure 3(a)). The carbonyl band centered at 1732 cm^{-1} , representative of the ester groups, develops a small shoulder at lower frequencies, indicative of oxidation products (Figure 3(b)). Overall, these small changes in the FTIR spectra suggest that Lotryl[®] 35BA320 is a relatively stable polymer under indoor exposure conditions.

The strong absorption at 1160 cm^{-1} representative of the C–O bond in the ester group shows no change, indicating the light stability of the butyl acrylate ester side chain. Overall, these minimal changes demonstrate the relative stability of the polymer.

As reported previously for the degradation of linear low-density polyethylene, main chain cleavage results in the formation of vinyl end groups when exposed to a medium pressure mercury lamp [40]. However, if vinyl end groups were formed during irradiation, absorption peaks around 910 and 990 cm^{-1} related to the terminal C=C double bonds (vinyl end groups) would be observed. But clearly no main chain cleavage occurs. Changes in the molecular weight distribution of the copolymer after the aging process further elucidate the observations in FTIR.

After aging, the SEC chromatogram of the soluble fraction of the EBA copolymer shows a shift to longer retention times (Figure 4).

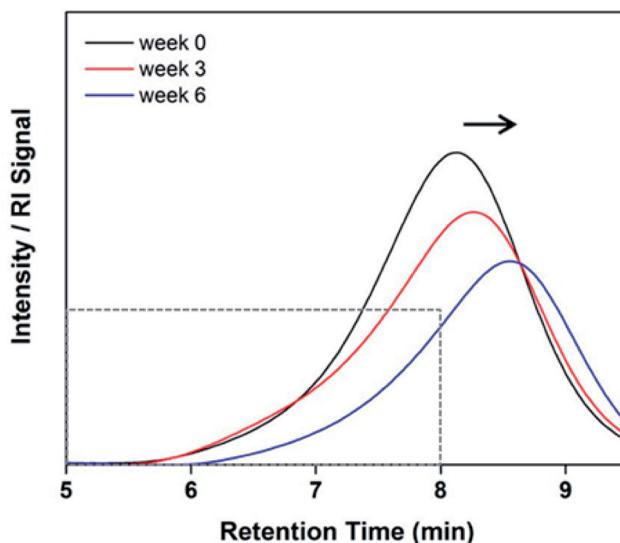


Figure 4. SEC chromatograms of unaged (black), week 3 (red), and week 6 (blue) of Lotryl® 35BA320.

Table 3. Molecular weight averages of the soluble fraction of Lotryl® 35BA320 during accelerated aging. Data gathered from aging of copolymer alone [8, 35].

Lotryl® 35AB320	Irradiation (weeks)	M_n	M_w	PDI (M_w/M_n)	Gel content (%)
Unstabilized	0	30,000	100,000	3.3	–
	3	27,000	111,000	4.1	–
	6	16,000	60,000	3.8	19

Additionally, the integrated area of the week 6 chromatogram is smaller than that of the unaged material. It has been reported for EVA copolymers with a low percentage of vinyl acetate that photodegradation may result in insoluble fractions. It is possible that the photodegradation of EBA copolymers is similar to EVA, producing insoluble material upon irradiation.

To determine if any insoluble copolymer fraction was present, the gel content of films at week 6 of aging was measured. It was determined for Lotryl® 35BA320 that ~19% of the material did not dissolve in THF for the week 6 aged sample, Table 3. This loss of soluble material explains the decrease in signal area in the SEC chromatograms, as it represents only the soluble fraction (Figure 4). Cross-linking of copolymer chains is the likely cause. The shift to lower molecular weights in the SEC is, therefore, attributed to the fact that the higher molecular weight, insoluble fractions are not represented in the chromatogram of the aged material. The cast copolymer films of Lotryl® 35BA320 remains transparent during aging with no visible changes in color or opacity.

The higher molecular weight copolymer Lotryl® 35BA40 undergoes similar changes in FTIR and SEC (Figure S1). However, light exposure has a larger impact on the film solubility in THF (Table S4). Lotryl® 35BA40 undergoes more severe crosslinking at 6 weeks, resulting in an 87% gel content with the area in the chromatogram representing the minor, soluble copolymer fraction. Since Lotryl® 35BA40

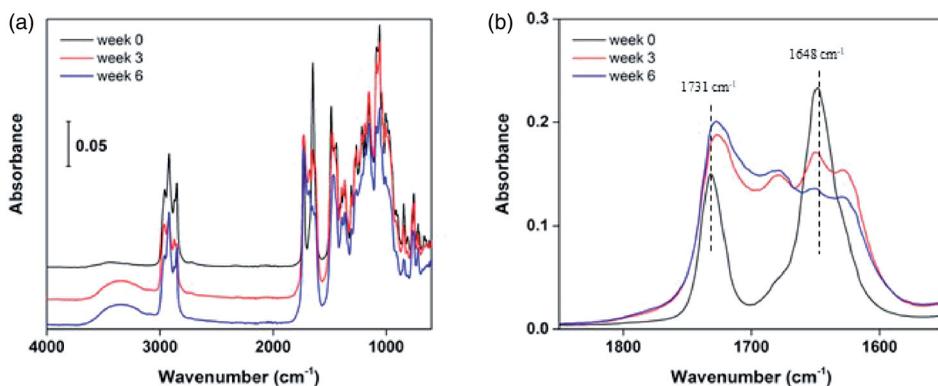


Figure 5. FTIR of unaged (black), week 3 (red), and week 6 (blue) aged polymer blend Lotryl[®] 35BA320/Laropal[®] A 81. (a) FTIR spectra from 4000 to 650 cm^{-1} . (b) FTIR spectra of the carbonyl region between 1850 and 1550 cm^{-1} .

is higher in molecular weight than Lotryl[®] 35BA320, crosslinking may have a greater effect on solubility.

This loss of copolymer solubility for aged EBA when used as an adhesive consolidant presents a concern as it would impede future consolidation treatments and, if required, may prevent easy removal of the adhesive in the conservation of art materials.

3.4. Polymer blend Lotryl[®] 35BA320/Laropal[®] A 81

Upon irradiation, several changes are observed by FTIR of the polymer blend (1:1 weight: weight) Lotryl[®] 35BA320/Laropal[®] A 81 (Figure 5(a)). Broad O–H absorption bands appear in the hydroxyl region between 3600 and 3050 cm^{-1} over time. The two distinct carbonyl absorption bands at 1731 cm^{-1} and 1648 cm^{-1} , with the former caused by the butyl acrylate groups in EBA and the amide group in Laropal[®] A 81, and the latter by the amide group in Laropal[®] A 81, become hidden at weeks 3 and 6 of aging due to significant band broadening within this region due to the formation of new absorption bands (Figure 5(b)). These changes are evidence of photo-oxidation and the formation of new hydroxyl and carbonyl species. However, the visually transparent films do not show any visible changes in color or opacity after aging.

These FTIR results are comparable to those for Laropal[®] A 81 alone, as previously reported [8]. Previous studies of this urea-aldehyde resin have also shown the formation of oxidation products [8,24,25]. The observed changes in the FTIR spectrum of the polymer blend are most likely primarily from Laropal[®] A 81 oxidation products.

Changes in the molecular weight distribution were observed by SEC for the aged polymer blend Lotryl[®] 35BA320/Laropal[®] A 81 (Figure 6(a)). The blend shifts to lower molecular weight upon aging. The molecular weight for the soluble fractions of the Lotryl[®] 35BA320 copolymer decreased after 6 weeks. After 6 weeks, a significant insoluble fraction has formed due to crosslinking.

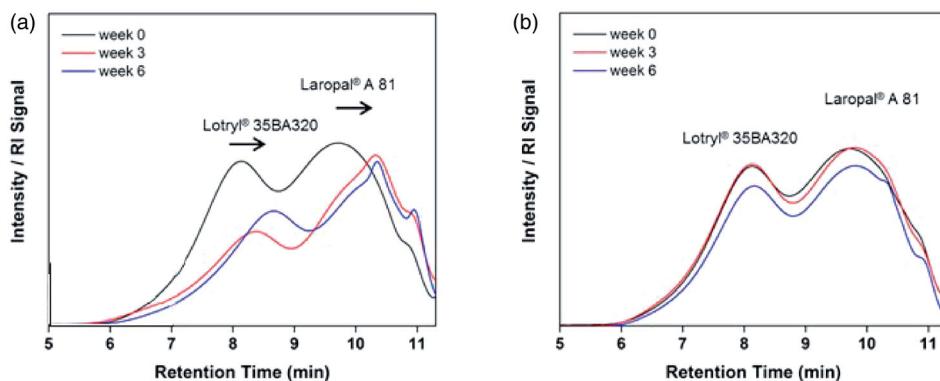


Figure 6. SEC chromatograms of unaged (black), week 3 (red), and week 6 (blue) of Lotryl® 35BA320/Laropal® A 81. (a) Unstabilized and (b) stabilized with Tinuvin® 292 (2 wt%).

The gel content of the Lotryl® 35BA320/Laropal® A 81 blend (1:1 weight/weight) after 6 weeks was found to be $\sim 9\%$, roughly half the measured gel content of the copolymer alone. Assuming no changes occur to the film mass from irradiation, and that Laropal® A 81 does not become insoluble or cross-link with the insoluble EBA copolymer, it is estimated that $\sim 18\%$ of the EBA polymer gels. We arrive at this estimation considering that the copolymer constitutes 50% of the weight in the blend and 9% of the blend becomes insoluble. The estimated gel content of the insoluble EBA copolymer of the blend is comparable to the measured gel content of the insoluble EBA copolymer alone, reported in Table 3. This suggests that the amount of cross-linked Lotryl® 35BA320 is not influenced by the presence of the low molecular weight resin Laropal® A 81. Furthermore, the changes of Laropal® A 81 within the blend were comparable to previous reports, which also indicated a shift to lower molecular weights.

Inhibition of the changes in the polymer blends by incorporation of a hindered amine light stabilizer (HALS) was investigated. HALS are known to inhibit degradation of various polymers [30–32]. They have already proven to be effective in cultural heritage materials [8,14,29].

The HALS Tinuvin® 292 was added to the polymer blend at 2% (weight/weight). Observed by SEC, the blend of Lotryl® 35BA320/Laropal® A81 was effectively stabilized by Tinuvin® 292, even after 6 weeks of irradiation (Figure 6(b)), showing minimal changes in the molecular weight distribution and average molecular weights of both components. Furthermore, the blend exhibited 0% gel content after 6 weeks of accelerated aging. The FTIR spectra of the Tinuvin® stabilized blends are shown in Figures 7(a,b). They are in agreement with the above observation. The graphs show that after 3 and 6 weeks of aging the absorption bands at 1731 cm^{-1} and 1648 cm^{-1} are more distinct than in the unaged blend due to fewer photo-oxidation products, even though some changes can be observed in the carbonyl region. This suggests that photo-chemical changes occur via a free radical process and that Tinuvin® 292 is an effective stabilizer for these blends in indoor museum conditions.

The blend of the higher molecular weight EBA Lotryl® 35BA40 copolymer with Laropal® A 81 (1:1 weight/weight) was also aged and examined using FTIR and SEC

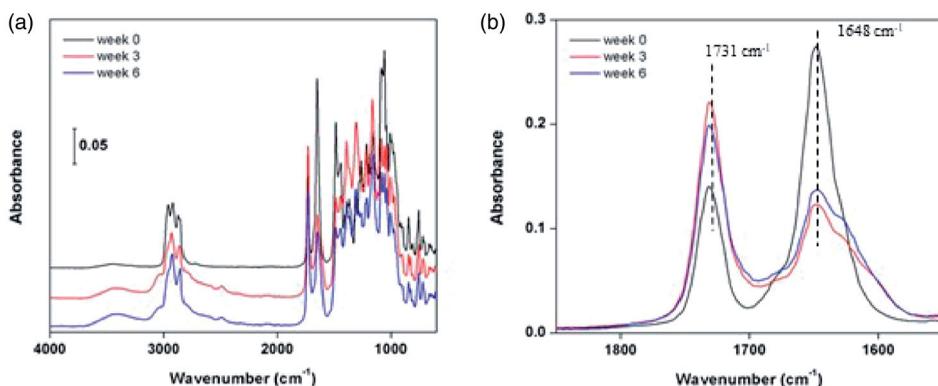


Figure 7. (a) FTIR of unaged (black), week 3 (red), and week 6 (blue) aged polymer blend Lotryl[®] 35BA320/Laropal[®] A 81 with the addition of 2wt% of Tinuvin. (a) FTIR spectra from 4000 to 650 cm^{-1} . (b) FTIR spectra of the carbonyl region between 1850 and 1550 cm^{-1} .

(Figure S2). The SEC data for both components are reported in Tables S2 and S3. The results are analogous to those for the Lotryl[®] 35BA320/Laropal[®] A 81 blend, suggestion that the oxidation of Laropal[®] A 81 is independent of the EBA copolymer molecular weight.

The higher molecular weight Lotryl[®] 35BA40 copolymer blended with Laropal[®] A 81 exhibited similar stability in SEC after 6 weeks of aging as the aged EBA copolymer alone, Tables S1 and S2, reflected in the gel content of 41%. Assuming there are no significant changes in film mass during irradiation and that Laropal[®] A 81 does not become insoluble or cross-link with the insoluble EBA. This suggests that the photochemical stability of the EBA copolymers is not influenced by the addition of Laropal[®] A 81.

The Lotryl[®] 35BA40/Laropal[®] A 81 blend was also mixed with 2 wt% Tinuvin[®] 292. After aging, SEC showed a significant improvement (Figure S2(d)) in the molecular weight distribution when compared to the unstabilized blend (Figure S2(C)). The 6 weeks aged sample fully dissolved in THF and exhibited 0% gel content. Along with the SEC data, this provides strong evidence that the Tinuvin[®] 292 is capable of stabilizing EBA/Laropal[®] A 81 blends.

3.5. Binary mixture of Lotryl[®] 35BA320 and Regalrez[®] 1094

Structural changes were observed in the aged polymer blend of Lotryl[®] 35BA320/Regalrez[®] 1094 when compared to the unaged blend. FTIR shows a slight increase in absorption in the hydroxyl region between 3600 and 3000 cm^{-1} , evidence of photo-oxidation (Figure 8(a)). The carbonyl peak at 1732 cm^{-1} increases and broadens (Figure 8(b)). At first glance, these structural changes suggest formation of new oxidation products.

However, the degree of oxidation may not be as substantial as the changes in the carbonyl region (1850–1550 cm^{-1}) suggest. The FTIR of the unaged, week 0 blend exhibits only a minor carbonyl absorption band at 1732 cm^{-1} and a minor C–O absorption band at 1160 cm^{-1} (Figure 8(a)). These intensities are much lower than the relevant absorption

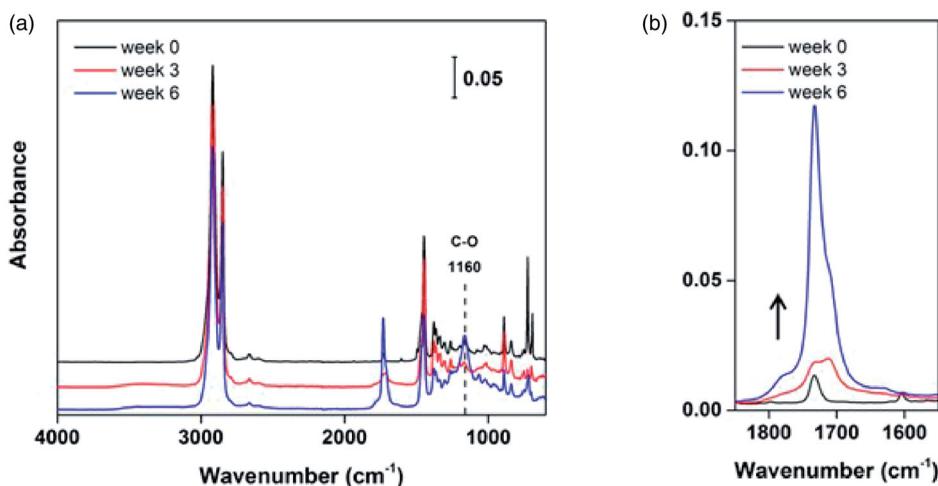


Figure 8. FTIR of unaged (black), week 3 (red), and week 6 (blue) aged polymer blend Lotryl[®] 35BA320/Regalrez[®] 1094. (a) Full FTIR spectra from 4000 to 650 cm⁻¹. Dashed line at 1160 cm⁻¹ highlights the C–O absorption band. (b) FTIR spectra of the carbonyl region between 1850 and 1550 cm⁻¹.

bands observed in the unaged, week 0 of the Lotryl[®] 35BA320 copolymer alone sample (Figure 3). This suggests that the carbonyl region intensity is reduced due to the shielding effect of Regalrez[®] 1094. Considering with the fact that the Lotryl[®] 35BA320/Regalrez[®] 1094 (1:1 weight/weight) films were visually slightly opaque when solidified at room temperature, there is ample evidence that this is the effect of the phase separated part of the Regalrez[®] 1094 partly migrated to the film surface.

The FTIR data, obtained *via* ATR, provide spectral information up to a depth of 0.5–3.0 μm [41]. If Regalrez[®] 1094 will be more concentrated at the air/film interface, this would explain the reduced intensity of C–O (1160 cm⁻¹) and C=O (1732 cm⁻¹) absorptions bands compared to the ones found in the EBA copolymer-alone spectra (Figure 3). This is analogous to similar reports where low molecular weight additives migrate out of the bulk material and concentrate at the surface [23,42].

After 6 weeks of aging, the FTIR spectrum of this mixture looks more like that of the Lotryl[®] 35BA320 alone spectrum (Figure 3), with greater peak intensities at 1732 cm⁻¹ and 1160 cm⁻¹ due to the ester groups. This suggests that the copolymer containing the butyl ester side chains is close enough to the surface to be detected by ATR. The shielding effect after 3 weeks of aging is analogous to our previously reported study on the accelerated light-aging of Regalrez[®] 1094 combined with acrylate block copolymers.

The changes in molecular weight distribution of Lotryl[®] 35BA320/Regalrez[®] 1094 were observed by SEC (Figure 9(a)). After 3 weeks of irradiation, there is a notable shift towards lower molecular weight. After 6 weeks, a further shift to lower molecular weight occurs. Gel content measurements after week 6 revealed that the aged copolymer still completely dissolved into THF, with a 0% gel content (Table 4). This is in contrast to the measured gel content of aged Lotryl[®] 35BA320 alone at 19% non-

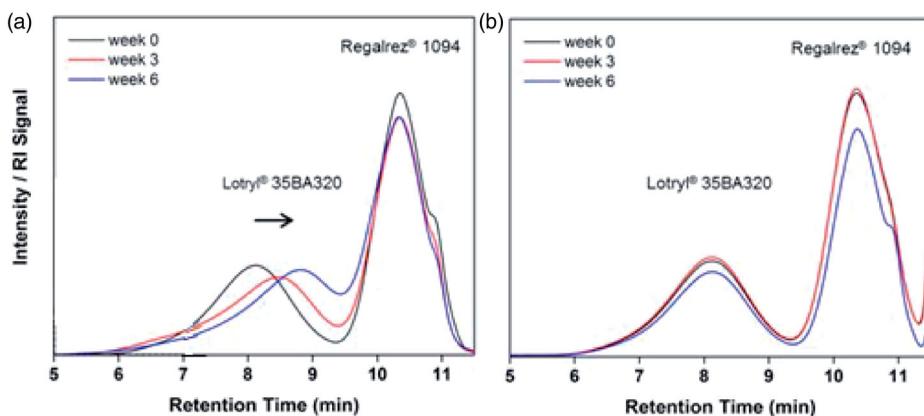


Figure 9. (a) SEC chromatograms of unaged versus aged polymer blend Lotryl[®] LA35BA320/Regalrez[®] 1094. (b) SEC of Lotryl[®] 3BA320/Regalrez[®] 1094 unaged versus aged with the addition of Tinuvin[®] 292 (2 wt%).

Table 4. Molecular weight averages of Lotryl[®] 35BA320 during accelerated aging.

Lotryl [®] 35BA320	Irradiation (weeks)	M_n	M_w	PDI (M_w/M_n)	Gel content (%)
Unstabilized	0	30	100	3.3	0
	3	23	115	5.0	0
	6	16	93	5.8	0

Data gathered from blends containing Lotryl[®] 35BA320/Regalrez[®] 1094, using deconvolution software [8, 35].

dissolved gel content. This further supports the idea that EBA blends containing Regalrez[®] 1094 are less susceptible to photochemical changes.

Tinuvin[®] 292 was added to the polymer blend. After 3 weeks of irradiation, Lotryl[®] 35BA320/Regalrez[®] 1094 was stabilized with no detectable changes in molecular weight distribution (Figure 9(b)). Within the stabilized polymer blend, Regalrez[®] 1094 exhibited excellent photostability upon irradiation, as noted by minimal changes in the chromatogram (Figure 9(b)). Average molecular weights exhibited only very slight changes in M_n and M_w with irradiation, PDI values are comparable to the unaged resin, and without gel content either with or without Tinuvin[®] 292. This is in agreement with previous reports on the photostability of this hydrogenated hydrocarbon resin [8,18,26,43].

After 6 weeks of irradiation, only minor changes were detected in the molecular weight distributions. These results are in agreement with previous reports that Tinuvin[®] 292 effectively stabilizes Regalrez[®] 1094 [8,24,25]. These results, again, suggest that the degradation is the result of a free radical mechanism that can be prevented by inclusion of Tinuvin[®] 292.

The higher molecular weight Lotryl[®] 35BA40/Regalrez[®] 1094 blend was also aged and analyzed (Figure S3). The dried films were visually opaque. The resulting FTIR spectrum for the unaged blend was similar to the lower molecular weight Lotryl[®] 35BA320/Regalrez[®] 1094 unaged blend, featuring a FTIR spectrum comparable to previously reported unaged Regalrez[®] 1094 [8].

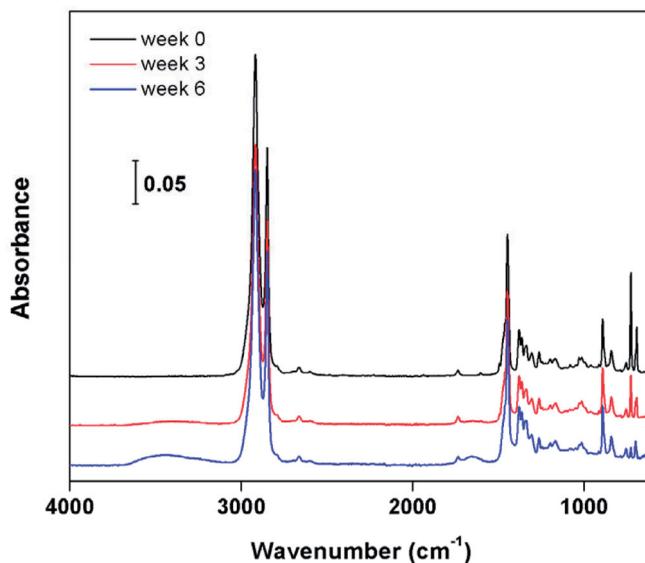


Figure 10. Full FTIR spectra from 4000 to 650 cm^{-1} of unaged (black), week 3 (red), and week 6 (blue) aged polymer blend of Lotryl[®] 35BA320/Regalrez[®] 1094 with the addition of 2 wt% of Tinuvin.

The SEC of the blends were also analyzed and the results are reported in [Tables S4 and S5](#). The EBA copolymer Lotryl[®] 35BA40 exhibited minor changes with shifts to lower molecular weights while the low molecular resin Regalrez[®] 1094 only exhibited minor changes. The gel content was determined to be 43% in the blend. Using the same assumptions as before, this suggests that $\sim 86\%$ of the Lotryl[®] 35BA40 copolymer becomes insoluble after aging due to cross-linking. This is comparable to the 87% gel content found for the Lotryl[®] 35BA40 copolymer aged alone ([Table S1](#)).

To help prevent degradation, 2 wt% Tinuvin[®] 292 was added to the Lotryl[®] 35BA40/Regalrez[®] blend. As seen in [Figures S3e and Figure 10](#), the addition of the stabilizer was effective in respectively preventing drastic changes to the average molecular weights ([Tables S4–S5](#)) and changes in the FTIR absorption spectra. The addition of Tinuvin[®] 292 resulted in a soluble film with 0% gel content. This further supports the suggested idea that EBA undergoes photochemical changes *via* a free radical process which can be prevented using Tinuvin[®] 292.

3.6. T-Peel strength of polymer blends

The peel strength of the polymer blends was investigated to provide more insight into their potential use as consolidating adhesives ([Figure 11](#)). During consolidation of fragile paint on an object, typically the conservator will apply the adhesive in between paint flakes or within cracked layers. Therefore, the mechanical strength of polymer materials was measured when bonded between two flexible painted substrates in peel, not only for best representation of the forces working on the adhesive layer, but also to determine the weakest part of the adhesive bond as a whole. A fast drying alkyd paint from Winsor & Newton was chosen to represent a typical modern paint layer.

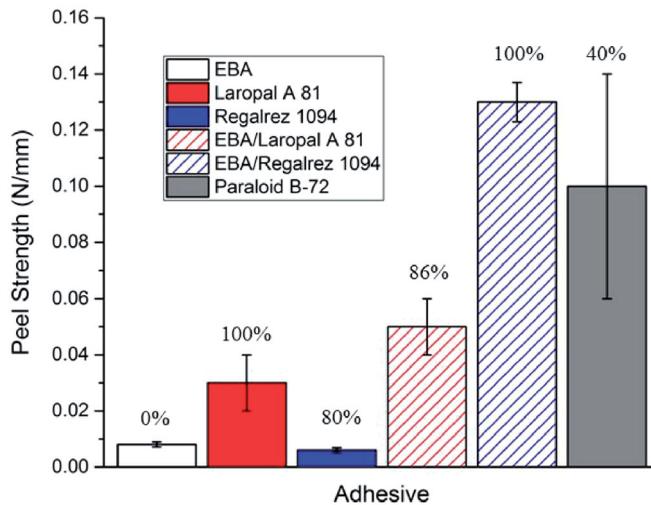


Figure 11. T-Peel strength of EBA, low molecular weight tackifiers, polymer blends, and Paraloid™ B-72. The graph also shows the percentages of cohesive failure on top of the bars. Values for Paraloid™ B-72 were previously reported [8].

The T-peel strength data, including the percentage of cohesive failure of Lotryl® 35BA320 blended with low molecular weight resins Laropal® A 81 and Regalrez® 1094 and of the individual components of the blends, are displayed in Figure 11.

Regalrez® 1094 alone showed a peel strength of 0.006 N/mm with a 80% cohesive failure in the adhesive layer due to a rather good adhesion to the surface. A value which is comparable to that of the EBA, Lotryl® 35BA320, alone (0.008 N/mm). However, the EBA was showing very poor adhesion with 100% adhesive failure.

When comparing the above peel strength values (shown in Figure 11) of the pristine EBA copolymer with the binary blends, it can be seen that the peel strengths of EBA/Laropal® A81 and the EBA/Regalrez®1094 blends increase to 0.05 and 0.13 N/mm, respectively. This can be attributed to the improved wetting and compatibility of the mixtures with the adherend surface resulting in better adhesion and higher peel strength of the binary blends compared to pristine EBA [16]. Moreover, the improved wetting and compatibility of the binary blends with the adherend surface can be confirmed by the analysis of the failure mode of the bonded area after testing; as indicated in Figure 11, the mode of failure shifts from 100% adhesive failure in case of EBA alone to 86% cohesive failure in case of the EBA/Laropal®A81 blend, whilst the EBA/Regalrez® blend exhibits a 100% cohesive failure inside the adhesive layer.

The improved wetting can also be the effect of the reduction in viscosity and higher mobility (see next section) of the polymer chains in the adhesive mixtures due to the addition of low molecular weight molecules allowing the chains to better penetrate into the pores and crevices of the painted surface. The viscosity reduction and, hence, increase of mobility of the binary mixture is expected to be more prominent in case of the EBA/Regalrez® 1094 blend due to the lower molecular weight of this resin.

As shown by the DSC analysis, the addition of a non polar low molecular weight resin such as Regalrez® 1094 interferes with the crystal size and the degree of crystallinity of the non-polar ethylene domains of the EBA [19,37,44,45]. Crystalline domains

act as physical cross-links improving the mechanical strength of the polymer systems. Hence, it is believed that the higher crystallinity of the EBA/Regalrez[®] 1094 mixture compared to EBA/Laropal[®] A 81 (shown by DSC analysis) is an important factor for the higher cohesive strength and a higher peel strength value.

Furthermore, within the standard deviation, the EBA/Regalrez[®] 1094 blend showed comparable T-peel strength to the commercially available Paraloid[™] B-72, a transparent thermoplastic acrylic resin, used as a consolidating adhesive by conservator-restorers for paintings, glass, ceramics, fossils, etc. [7].

3.7. Contact angle measurements

Contact angle measurements were used to obtain the surface energy of the adherends used in the T-Peel tests. The alkyd painted ground layer surface showed a surface energy of 38.5 ± 3.5 mN/m, which is low, with a minor polar contribution of only 0.5 ± 0.1 mN/m. This implicates that the surface tension of the solvent of the heat seal adhesive during application for interfacial contact should at least be lower (toluene 28.5 mN/m, 20 °C) [44].

The T-Peel strength value of Laropal[®] A81 on the acrylic ground layer was found to be around 18 times higher than on alkyd paint (surface energy of the ground layer was 50 ± 2 mN/m, with a much higher polar contribution of 10 ± 0.5 mN/m). This increase of bond strength is most possibly due to the increase of polar interactions [37,44,46].

3.8. Viscosity

The test results (Figures 12 and Figure S4) show the evolution of the dynamic viscosity with different concentrations (weight/weight %), compositions and temperatures. The

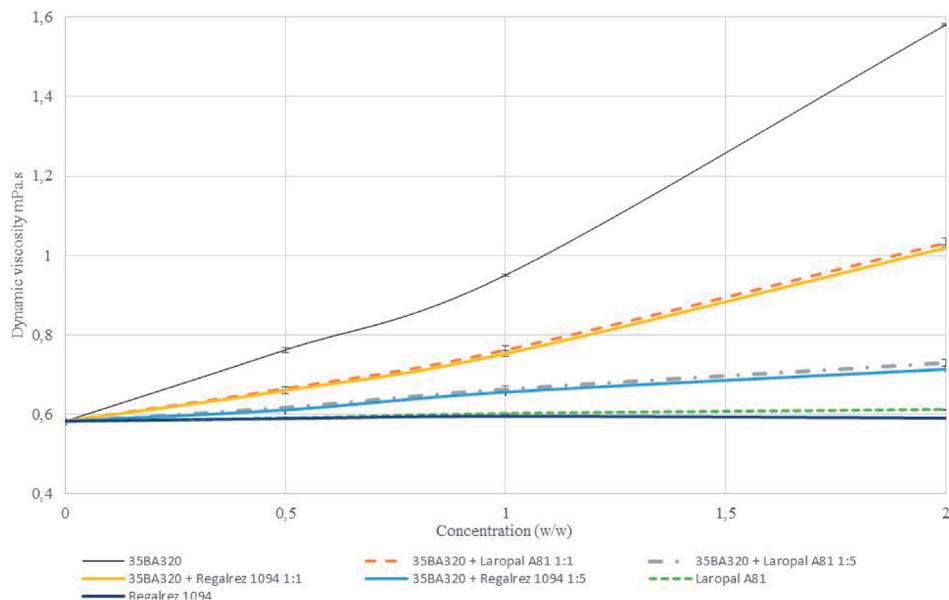


Figure 12. The Evolution of the dynamic viscosity of Lotryl[®] 35BA 320 Blends and its separate constituents at 25 °C as a function of the concentration in toluene.

standard deviation was generally found to be less than 0.1%, and, therefore, not visible. The Lotryl[®] 35BA320 system alone showed the highest dynamic viscosity, strongly increasing with an increasing concentration in toluene or decreasing temperature and decreasing with an increasing concentration of either LMWRs. The results further show that the viscosity of all blends decreased significantly when the temperature is increased.

When the LMWs were considered alone, it was noticed that the dynamic viscosity was close to the viscosity of toluene and increased linearly (but slowly) with an increasing concentration, but decreasing with increasing temperature.

The dynamic viscosity data at both 25 °C and 60 °C for the blends of Lotryl[®] 35BA320 with Laropal[®] A81 and Regalrez[®] 1094 at the same weight ratios were found to be very close, often overlapping, and increasing slowly with an increase of the LMW concentration, though all lower at 60 °C. These results clearly show the lowering of the viscosity by addition of LMW resins.

3.9. Consolidation experiments

The most valuable blend properties defined by conservators were found to be the strength by which the adhesive flake adhered to the ground layer and the combination of flow and gloss of the consolidant. The outcome of the tests which determined the best performing blends was found to be strongly influenced by personal feel and consolidating conditions like temperature, which influences the viscosity (of the blends). Though the best performing blends were found to be:

- On the gouache mock-up: Laropal[®] 35BA 320 1:1 blend with Laropal[®] A81 (weight/weight).
- On the alkyd oil paint mock-up: Laropal[®] 35BA 320/Laropal[®] A81 both 1:1 and 1:5 ratios (weight/weight).
- On the old dummy/sample of the 1961 oil painting: Laropal[®] 35BA 320/Acrylic Regalrez[®] 1094 1:1 ratio (weight/weight).

The overall conservation test results showed that the viscosities of the blends were found to be tuneable, while maintaining appreciable adhesion. Besides this, the blends acted as a filler material due to the bulky property of the EBA copolymer.

4. Conclusions

Commercially available ethylene butyl acrylate copolymers, Lotryl[®] 35BA320 and Lotryl[®] 35BA40, were blended with low molecular weight resins, Laropal[®] A 81 and Regalrez[®] 1094, to investigate their long-term photo-stability as new, potential material for consolidating adhesives. Results presented here prove that upon irradiation in simulated indoor museum conditions the copolymer Lotryl[®] 35BA320 undergoes photo-degradation by cross-linking reactions. Similar degradation occurs with the higher molecular weight copolymer Lotryl[®] 35BA40 conditions. Gel content

experiments revealed that a fraction of EBA copolymers become insoluble in THF after irradiation.

When blended with Laropal[®] A81, the EBA copolymers exhibited comparable degradation to the blends without the presence of the urea-aldehyde low molecular weight resin. The addition of Regalrez[®] 1094 to the Lotryl[®] 35BA40 copolymer blend exhibited similar photo-degradation and resulted in insoluble gel content. However, the presence of Regalrez[®] 1094 imparted a degree of stability to the lower molecular weight EBA copolymer, Lotryl[®] 35BA320, most possibly a result of light scattering by the opaque samples caused by a partial phase separation. This resulted in a complete THF-soluble material even after 6 weeks of aging.

Test results show that addition of a hindered amine light stabilizer halted photo-degradation. Data were obtained in a simulated indoor condition of daylight passing through window glass at 40 °C. Consequently, it is recommended to add Tinuvin[®] 292 to EBA copolymer blends to achieve maximum photo-stability.

DSC data showed that the components of the binary mixtures of EBA with both Laropal[®] A81 and Regalrez[®] 1094 demonstrated limited miscibility of the 1:1 binary mixtures and showcased by similar T_g values to the pure EBA copolymer, though the melting temperature of EBA/Regalrez[®] 1094 showed a slight reduction, possibly indicating a smaller crystal size. More importantly, the degree of crystallinity of the EBA was significantly improved by the Regalrez resin, leading to a higher cohesive, and, as a result, higher peel strength value for this mixture. Besides this, the improved wetting and compatibility of the binary blends with the low energy and low polarity alkyd painted adherend surface showed an increase of the cohesive failure mode.

The adhesive blends were found to exhibit good to excellent adhesion to alkyd painted surfaces. The hard polyethylene crystalline backbone of the EBA has obtained some interference due to the low molecular weight molecules changing the size and mobility of the crystalline domains. Consequently, the peel strength of the binary EBA blends dramatically increased. Furthermore, EBA/Regalrez[®] 1094 exhibited the highest measured average peel strength and a tuneable viscosity, suggesting that this material shows to be an interesting blend for further research for properties necessary for consolidating work.

Consolidation tests on mock-up and dummy paintings done by professional conservators, showed the applicability of a number of blends. Although two extreme ratios of polymer to low molecular weight resin were used for the laboratory experiments, other ratios may of course prove to be beneficial in actual conservation treatments.

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