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The photo-stability of acrylic tri-block copolymer blends for the consolidation of cultural heritage

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ABSTRACT

A variety of adhesives are used for the conservation of paintings. These materials include natural adhesives such as animal glues, waxes, and gums which may chemically degrade over time resulting in unwanted discoloration and mechanical failure. Synthetic adhesives have been introduced to address these concerns. However, most consolidating adhesives have not been specifically formulated and tested to meet the high demands of conservation, ultimately resulting in undesirable physical and mechanical properties. Additionally, some synthetic adhesives are less stable and may cross-link making it difficult to remove years after application. This paper investigates the photo-stability of commercially available tri-block acrylic copolymers (PMMA-PnBA-PMMA) to assess their potential long-term serviceability as consolidants for flaking paint. These copolymers were combined with synthetic low molecular weight resins to reduce viscosity of the adhesive and provide tack. The polymer blends underwent accelerated aging under simulated indoor conditions. Blends were analysed for degradation using Fourier-transform infrared spectroscopy and size exclusion chromatography. Upon irradiation, acrylic copolymers (PMMA-PnBA-PMMA) undergo shifts to higher and lower molecular weight, suggesting that degradation occurs by polymer cross-linking and chain scission. Furthermore, the acrylic copolymer degradation rate was influenced by the type of low molecular weight resin. However, with the addition of a hindered amine light stabilizer these blends exhibited minimal changes in molecular weight. Lastly, the peel strength of the blends were investigated and shown to have comparable peel strength to a popular commercial material, Paraloid™ B-72, often used in consolidation thus showing their promise for use within cultural heritage.

1. Introduction

Paintings have a complex multi-layered composition made of various materials. Typically, a canvas painting is comprised of a textile support layer that is stretched on a wooden frame. A glue size layer is applied to the textile support, followed by a ground layer, several paint layers, and lastly, but not always, a varnish. All of these constituents have various chemical and mechanical properties and independently respond to environmental variations including temperature and relative humidity. During drying of the paint layers or from external environmental changes, stresses may occur within the material eventually resulting in delamination, cracking, or in severe cases powdering of the paint layers [1–3].

A wide variety of adhesives including natural materials such as gums, waxes, resins, and animal glues have been used for decades to adhere paint fragments or to consolidate fragile powdery material [4]. Although currently still in use, these natural adhesives may not possess the desired properties in penetration, adhesive strength and effect on optical appearance required for the restorative task at hand. Natural adhesives may degrade over time causing unwanted colour changes and mechanical failures [5].

Synthetic adhesives were introduced during the 20th century as an alternative to natural glues. Vinyl-acetate derived polymers such as poly(vinyl acetate), poly(vinyl alcohol), and polyvinyl butyral have been used as consolidating adhesives and are typically delivered in a solvent or as a dispersion [6,7]. Synthetic consolidating adhesives also include acrylic homopolymers and

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copolymers where the alkyl group is a methyl, ethyl, or n-butyl group as well as ethylene-based thermoplastic copolymers such as poly(ethylene-co-vinyl acetate) and poly(ethylene-co-butyl acrylate) [6–10]. Although some of these synthetic materials are more stable than their natural alternatives, they may still lack the required physical and mechanical properties for a consolidant [5,6].

Few attempts have been made to formulate material specifically for the field of cultural heritage [8,11] and several of the synthetic adhesives currently in use have never been investigated for their long-term stability as consolidating adhesives. Therefore, there is a great need to develop and evaluate new materials as consolidating adhesives based on their photo-stability. Furthermore, such materials could be used for other conservation needs, e.g. the relining of damaged canvases. However, several other factors need to be considered to meet the high demands of a consolidant for conservation.

It is important that a consolidant does not change the chemical, physical, and optical appearance of the object including gloss or colour saturation. While the consolidant should not influence the object's appearance, if the consolidant is not 100% optically clear, this does not exclude its potential use. The reason for this optical flexibility is due to the fact that during consolidation of paint flakes, the adhesive is placed between paint layers or inside cracks and should not be readily visible. Furthermore, consolidants should be ‘reversible’. This concept suggests that all or most of the adhesive can be removed, or at least reworked, although this demand may be difficult to meet in practice. This demand by itself limits the range of adhesives that can be used for restoration [3,6].

A synthetic material that has the potential to meet these stringent demands of durability for consolidant purposes is a tri-block acrylic copolymer, Kurarity™ from Kuraray Co., Ltd. Kurarity™ is an ABA type block copolymer consisting of hard end-blocks of methyl methacrylate and a soft mid-block of n-butyl acrylate (PMMA-PnBA-PMMA) (Fig. 1a) [12]. This type of tri-block acrylic based thermoplastic elastomer offers flexibility and adhesion all while being transparent. Due to their chemical nature, these copolymers can easily be removed after application with the assistance of an appropriate solvent. Additionally, according to Kuraray, the Kurarity™ series are UV and weather resistant [13].

As previously mentioned, consolidating adhesives must be relatively chemically stable for use in conservation. This paper investigates the photo-stability of Kurarity™ LA2140e and LA2330, both containing identical comonomer ratios but different molecular weights, to predict their long-term serviceability as a consolidant for deteriorating paint. Both acrylic-based copolymers contain ~23% PMMA and ~77% PnBA however, Kurarity™ LA2140e has a lower molecular weight than that of Kurarity™ LA2330 [12].

Additionally, polymer blends were formulated with commercially available low molecular weight resins, which may be added to adhesive systems to reduce viscosity of the adhesive, provide and increase tack, and dilute the polymer chain network [8,9,14]. Regalrez® 1094 (Fig. 1b), a hydrogenated hydrocarbon resin (Eastman), and Laropal® A 81 (Fig. 1c), a urea-aldehyde resin (BASF), were chosen for their relative stability and current use within cultural heritage as binding medium for retouching paints and picture varnishes [15–18]. While the structure of Regalrez® 1094 is well known, the structure of Laropal® A 81 in Fig. 1c is a proposed structure and is likely to be more complex [15,16]. In this paper the photo-stability of these low molecular weight resins blended with Kurarity™ LA2140e and LA2330 is investigated for potential use in cultural heritage. Additionally, a hindered amine light stabilizer, Tinuvin 292®, was added to the polymer blends in an effort to inhibit photo-degradation [19]. Furthermore, peel strength of the polymer blends were studied to investigate the feasibility for their intended use as consolidating adhesives.

2. Materials and methods

2.1. Materials

Acrylic block copolymers (PMMA-PnBA-PMMA), Kurarity™ LA2140e and LA2330, were obtained from Kuraray Europe GmbH. The low molecular weight resins Laropal® A 81 and Regalrez® 1094 and Paraloid™ B-72 were obtained from CTS Europe. According to

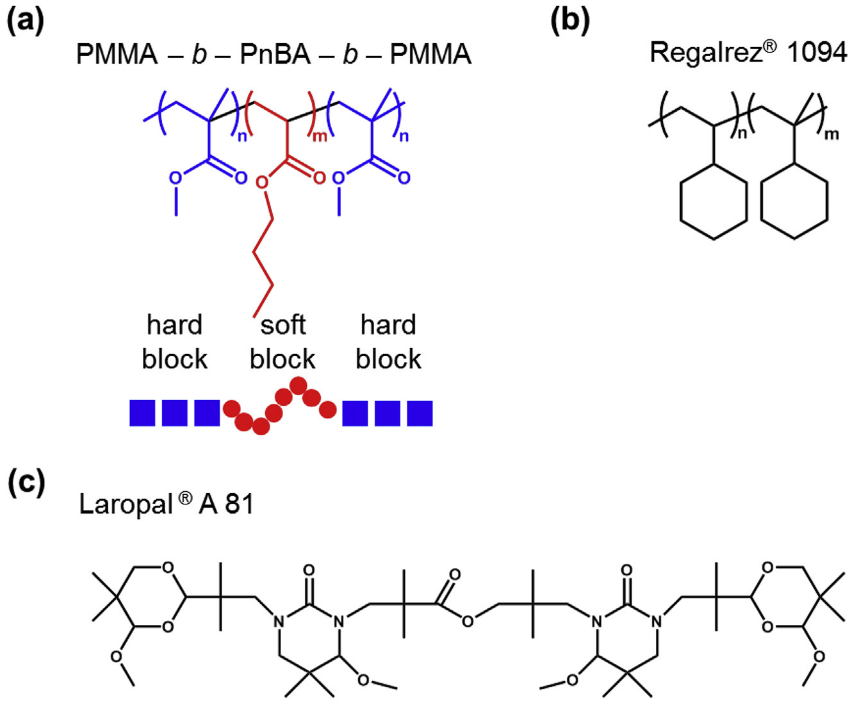

Fig. 1. Molecular structures of (a) Kurarity™ tri-block acrylic copolymer PMMA-PnBA-PMMA by Kuraray Co., Ltd. (b) Regalrez® 1094 and (c) The proposed structure of Laropal® A 81.

the manufacturers, the low molecular weight resins and acrylic block copolymers contain no added antioxidants or UV stabilizers. Tinuvin® 292 was purchased from Kremer Pigmente GmbH & Co. Reagent grade toluene and analytical grade tetrahydrofuran were purchased from VWR. Standard pre-ground canvas (Rijn Uni) was purchased from Claessens Canvas (Belgium). Winsor & Newton Griffin Alkyd Oil Paint Lemon Yellow series 1914722, pigment PY3 was obtained from Winsor & Newton. All chemicals, solvents, and materials were used as received.

2.2. Adhesive preparation

Polymer blends containing base copolymer Kurarity™ LA2140e or LA2330 and low molecular weight resin Laropal® A 81 or Regalrez® 1094 were prepared in toluene. Components were mixed in 1:1 ratio by dry weight of copolymer to dry weight of low molecular weight resin (weight/weight). Solutions were prepared at 20% of solid dry weight of base copolymer + low molecular weight resin per weight of solvent (weight/weight).

2.3. Film preparation for accelerated aging

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 0.8 mL were dispensed onto cleaned microscope slides and allowed to spread across the slides to form a film. Films were dried under ambient conditions, following a published procedure, while modifying the drying time to 4 weeks before beginning accelerated aging [20]. The drying time was increased by 4× to ensure no residual solvent remained. Although not controlled by direct means, this resulted in films of similar thickness, approximately 0.25 mm on average.

2.4. Accelerated aging

An Atlas Xenotest Alpha High Energy weathering instrument equipped with a Xenon arc lamp was used for accelerated aging of films. Experimental conditions were modified from ASTM D4459 and specific parameters are explained in detail here. Indoor conditions mimicking daylight passing through window glass were simulated. The irradiance level was held at 42 W/m^2 in the wavelength range of 300–400 nm. A Xenochrome 320 glass filter was used to block radiation below 320 nm. The test chamber temperature was 40 °C and the relative humidity was maintained at 40% during aging. All films were aged for a maximum of 6 weeks which is equivalent to 1008 h. The Xenon arc lamp has an illuminance of 105,087 lux compared with average museum conditions of 200 lux [21]. This increase in lux provides an environment that accelerates the degradation from light that may occur within indoor museum conditions. However, the increased temperature of the test chamber compared to indoor museum temperatures may also increase the overall rate of degradation [5]. Consequently, the results presented within this study may undergo increased deterioration than if temperatures were closer to museum conditions. This should be considered when comparing these presented results with other accelerated aging reports.

2.5. T-peel strength of adhesives

Test specimens were prepared using two flexible substrates of pre-ground canvas (305 mm × 25 mm). Alkyd oil paint was applied to the pre-ground surface using a precision thin film applicator of 200 μm and then dried at room temperature. Compressed air was used to remove any dust or debris from the substrate before bonding.

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 second substrate was placed atop the first to create a T-peel joint and a 200 g steel weight (280 mm × 25 mm) was applied. Weighted specimens were heated at 50 °C inside a vacuum oven for 1 h whereby the steel weight was removed and samples continued to dry for an additional 23 h at 50 °C. After this amount of time, the oven was evacuated and samples were heated at 50 °C under vacuum for an additional 6 days.

The relative peel strength of the adhesives were measured according to the ASTM standard test D 1876 using a Zwick 20 kN tensile machine (Zwick International, Ulm, Germany). A 1 kN load cell was used to measure the peel strength. 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 peel strength was determined.

2.6. Fourier-transform infrared spectroscopy (FTIR)

Films were analysed by Fourier-transform infrared spectroscopy (FTIR) using a Perkin Elmer Spectrum 100 FTIR spectrometer equipped with a universal attenuated total reflectance (ATR) sampling accessory and a ZnSe crystal. Data were collected at 16 scans with a resolution of 4 cm^{-1}. To take into account any surface heterogeneity, a minimum of three spectra in different areas were measured per sample. No notable changes 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)

Changes in molecular weight distribution of unaged and aged polymer blend films were monitored by size exclusion chromatography (SEC). A Shimadzu Prominence Ultra Fast Liquid Chromatography system equipped with a Shodex GPC LF-804 column (8.0 × 300.0 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. The instrument was calibrated using these standards with weight-average molecular weights (Mw) ranging from 1200 to 3,150,000 leading to a linear calibration plot (Fig. 2).

For the bimodal SEC chromatograms, Fityk software was used to deconvolute the peaks [22]. 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.

3. Results and discussion

The base copolymer Kurarity™ LA2140e and low molecular weight resins Laropal® A 81 and Regalrez® 1094 were aged separately under simulated indoor conditions. Additionally, polymer blends containing Kurarity™ LA2140e and the low molecular weight resins Laropal® A 81 and Regalrez® 1094 were aged during the same test run. Comparable blends containing the higher molecular weight base polymer, Kurarity™ LA2330, were also aged and data can be found in the Supplementary Data (Figs. S1–S6, Tables S1–S5).

Molecular weight averages were calculated for the unaged base copolymers and low molecular weight resins. Values of number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index ($PDI = M_w/M_n$) were calculated for all unaged bulk polymer blends (Table 1). It is important to note that

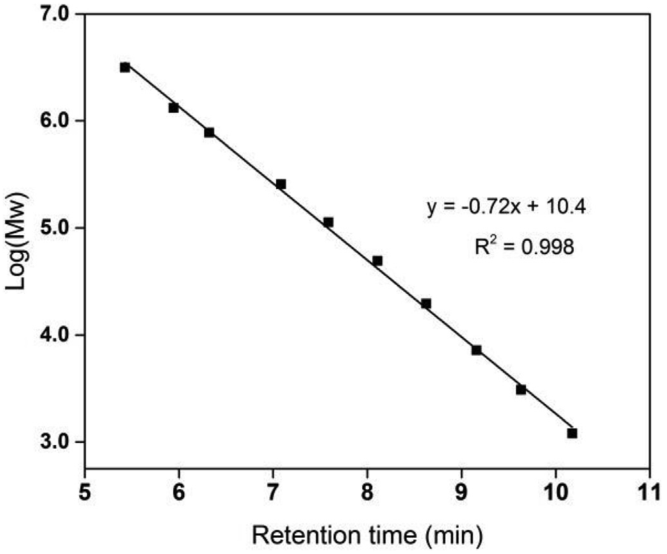

Fig. 2. Calibration curve derived from ten polystyrene standards with weight average molecular weights (M_w) ranging from 3,150,000 to 1200.

Table 1
Molecular weight averages of unaged bulk base copolymers and low molecular weight resins.

Polymer	M_n	M_w	PDI (M_w/M_n)
Kurarity™ LA2140e	52,000	63,000	1.2
Kurarity™ LA2330	88,000	107,000	1.2
Laropal® A 81	1500	3900	2.6
Regalrez® 1094	800	1200	1.5

average molecular weights for the low molecular weight resins fall outside the calibrated range, thus these values have been extrapolated from the polystyrene calibration curve. Approximate molecular weights in Table 1 are in agreement with literature reports for acrylic copolymers and low molecular weight resins [18,23].

3.1. Base copolymer Kurarity™ LA2140e and low molecular weight resins

3.1.1. Base copolymer Kurarity™ LA2140e alone

The acrylic block copolymer, Kurarity™ LA2140e, shows minimal structural changes as monitored by ATR-FTIR with irradiation of 6 weeks (~1004 h) in the Xenotest. There is evidence of minor oxidation of the copolymer with the formation of hydroxyl groups as supported by the broadening in absorption between 3800 and 3000 cm^{-1} (Fig. 3a). Additionally, the slight decrease in absorption of the main carbonyl peak at 1727 cm^{-1} suggests a loss of ester groups by side chain scission (Fig. 3b). However, since the carbonyl peak does not undergo significant changes and exhibits a slight increase in absorption at lower wavenumbers, this suggests that the formation of new oxidative products may compensate the loss of ester groups. Although minimal, these structural changes are further supported by changes in molecular weight distribution of the copolymer.

At 3 weeks of aging, the SEC chromatogram of LA2140e shows peak broadening with shifts to shorter and longer retention times, a result of cross-linking and chain scission reactions, respectively (Fig. 4). With longer irradiation time at week 6, the copolymer molecular weight distribution continues to broaden but shows much more extensive crosslinking. Changes in molecular weight averages for unaged and aged LA2140e are reported in Table 2. Similar changes in FTIR, SEC, and molecular weight averages were obtained for the higher molecular weight copolymer, LA2330, and are reported in the Supplementary Data (Fig. S2, Table S1).

These types of changes to the copolymer have been reported for similar materials [24–27]. Reports from literature detail similar photo-degradation mechanisms for acrylic and methacrylic homopolymers under conditions relevant to natural aging. Irradiating with wavelengths longer than 295 nm, Chiantore et al. [24,25] report that when alkyl groups are short (e.g. methyl or ethyl) for both acrylic and methacrylic polymers, degradation is more likely to occur via chain scission than cross-linking. However, with butyl ester side groups, these authors show that polymers undergo extensive cross-linking and chain scission [24–26].

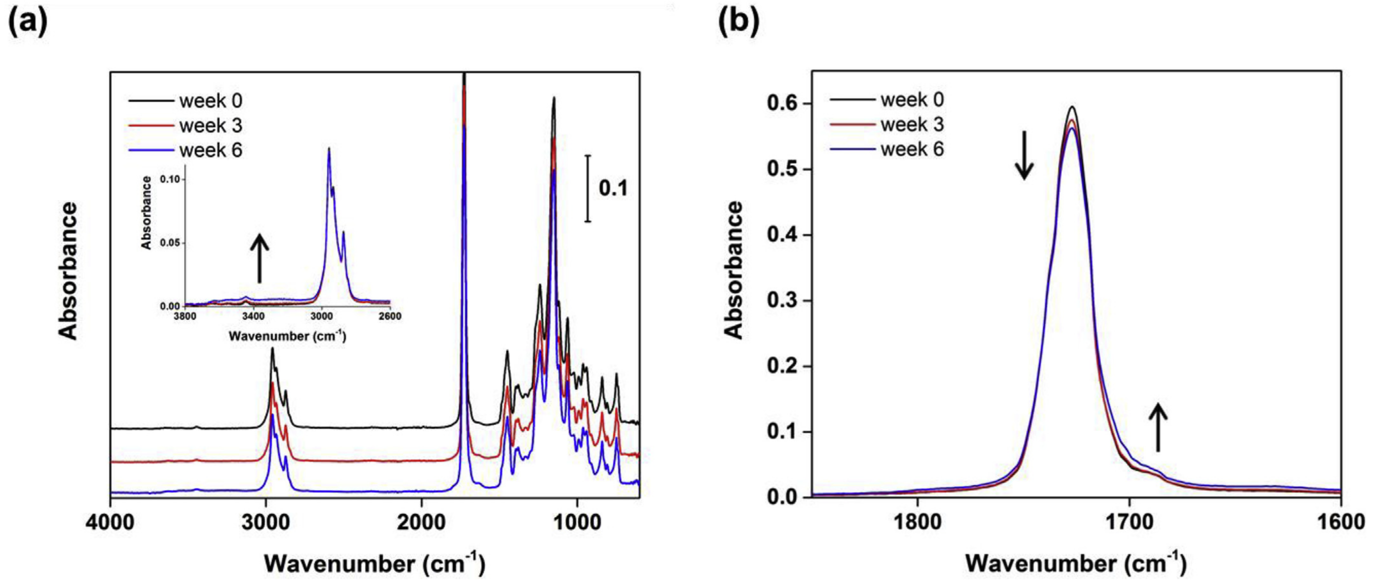

Fig. 3. FTIR spectra of unaged (black), week 3 (red), and week 6 (blue) aged copolymer A2140e. **(a)** Offset of FTIR spectra from 4000 to 650 cm^{-1} showing minimal structural changes upon aging with an inset of hydroxyl and C-H stretching regions from 3800 to 2600 cm^{-1}. **(b)** FTIR spectra of the carbonyl peak at 1727 cm^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

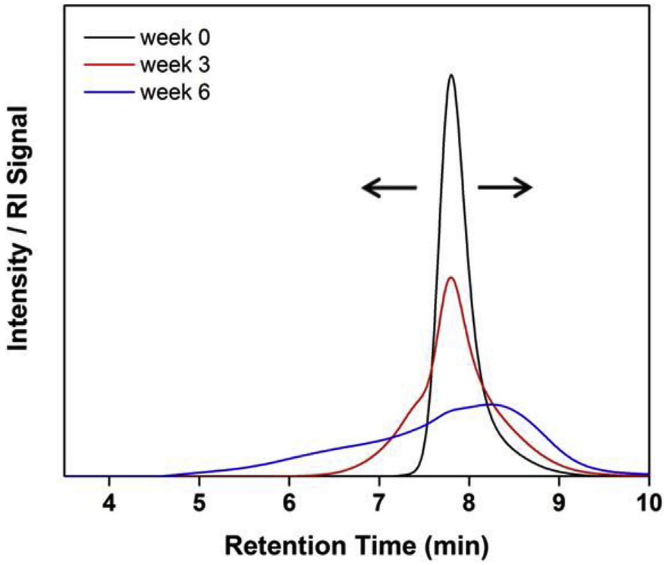

Fig. 4. SEC chromatograms of unaged (black), week 3 (red), and week 6 (blue) of LA2140e. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2
Molecular weight averages of LA2140e during accelerated aging. Data gathered from aging of copolymer LA2140e alone.

LA2140e	Irradiation (weeks)	M_n	M_w	PDI (M_w/M_n)
Unstabilized	0	52,000	63,000	1.2
	3	46,000	86,000	1.9
	6	32,000	354,000	11.1

In contrast, methacrylates such as poly(methyl methacrylate) (PMMA), are less susceptible to cross-linking and are relatively more stable compared to their polyacrylate counterparts. It has been reported that under accelerated aging conditions, extensive irradiation times are required before detecting any signs of oxidation to the polymer. Additionally, irradiation of PMMA must occur at wavelengths lower than 300 nm to observe degradation [27–29]. These findings suggested that PMMA is a relatively stable material especially when irradiated under simulated indoor conditions.

Our results on the accelerated aging of the PMMA-PnBA-PMMA tri-block copolymer LA2140e show extensive cross-linking and some polymer chain scission. The structural and molecular weight distribution changes observed upon irradiation of this copolymer is likely due to the photo-degradation of the poly(n-butyl acrylate) mid-block, and not the poly(methyl methacrylate) end-blocks. Although degradation is observed, with 6 weeks of irradiation the polymer film of LA2140e remains transparent. Photographs of unaged and aged copolymer films were taken (Fig. 5) and no changes in colour or opacity were detected.

3.1.2. Low molecular weight resins alone

Upon irradiation, when monitored by FTIR, Laropal® A 81 undergoes several structural changes. Notable changes are observed when comparing the unaged low molecular weight resin to the unaged resin (Fig. 6a). With irradiation there is the appearance of OH absorption bands in the hydroxyl region between 3650 and 3100 cm^{-1}. Furthermore, at 3 weeks of irradiation the two distinct carbonyl bands at 1730 and 1646 cm^{-1} show broadening and new absorption bands are formed within the region (Fig. 6b). These changes provide evidence of photo-oxidation and the formation of new carbonyl species, in agreement with previous reports on the photo-stability of Laropal® A 81 [15,30]. Upon aging, Laropal® A 81 undergoes photo-degradation forming new oxidative products which may include hydroxyl, ketones, and carboxylic functional groups.

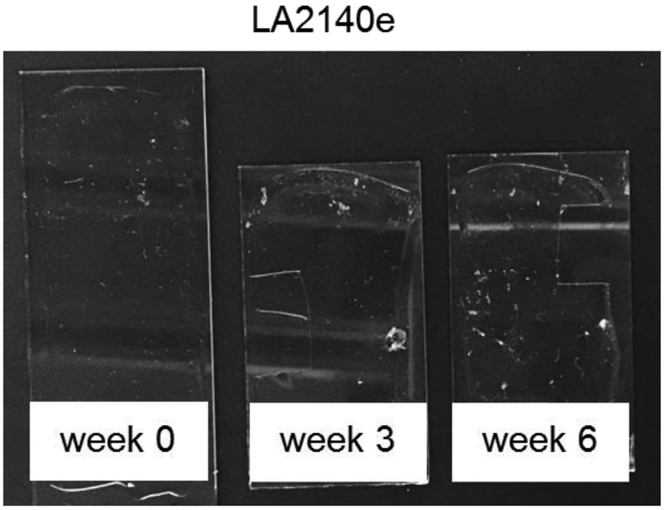

Fig. 5. Photographs taken with a black background of LA2140e dried films on microscope slides at week 0 (unaged), week 3, and week 6 aging. The contrast of the image was adjusted to help visualize the films. Areas where the film has been removed for analysis can be seen in the photographs.

Upon irradiation, changes in the molecular weight distribution of Laropal® A 81 were observed by SEC. Laropal® A 81 shifts to lower molecular weight when compared to the unaged resin (Fig. 6c). This is in full agreement with reported literature studies [15]. Additionally, changes in molecular weight further support the observed structural changes by FTIR. Specifically the formation of new absorption bands between 1730 and 1646 cm^{-1} are evidence for the formation of new oxidation products.

The low molecular weight resin, Regalrez® 1094, was also aged alone. Observed by FTIR, there is an increase in absorption of the hydroxyl region between 3650 and 3050 cm^{-1}, suggesting the formation of new O-H bonds (Fig. 7a). Furthermore, a new absorption band appears at 1712 cm^{-1} for the appearance of new C=O bonds. Additionally, there is a slight increase in absorption at 1200 cm^{-1}, indicating the appearance of C-O bonds. These structural changes suggest that upon irradiation the hydrogenated hydrocarbon resin undergoes photo-oxidation with the generation of new oxidation products. There is an observable decrease in absorption for the C-H stretching and bending regions, 3000 - 2750 cm^{-1} and 1500 - 1400 cm^{1}, respectively. It is uncertain exactly why these bands decrease so much in intensity, but it could be related to photo-oxidation of the material.

These results are further supported by the minor changes in SEC chromatograms for aged Regalrez® 1094 (Fig. 7b). A detectable change between the unaged sample and the 3 and 6 weeks aged sample can be noted, whereby the chromatogram shifts to a shorter retention time. This suggests that upon 3 weeks of irradiation, Regalrez® 1094 undergoes minor photo-degradation resulting in an increase in molecular weight probably in part due to the addition of oxygenated molecules and most possibly cross-linking. However, it is important to note that these changes are minor, agreeing with previously reported literature on the overall stability of Regalrez® 1094.

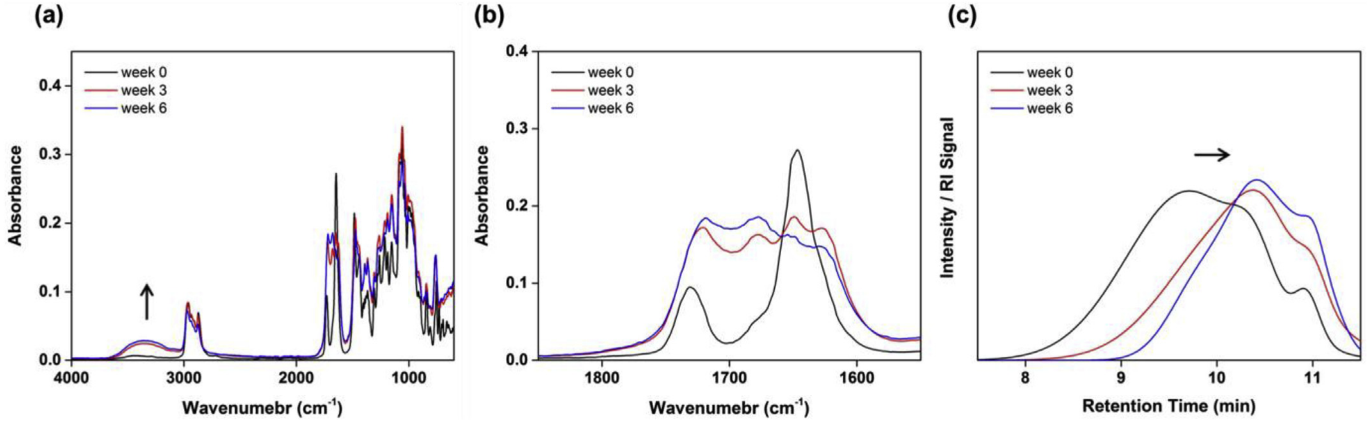

Fig. 6. (**a**) FTIR spectra of unaged (black), week 3 (red), and week 6 (blue) aged low molecular weight resin Laropal® A 81. (**b**) FTIR spectra of the carbonyl region. (**c**) SEC chromatograms of unaged versus aged Laropal® A 81. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.2. Polymer blend Kurarity™ LA2140e/Laropal® A 81

With the addition of Laropal® A 81, the polymer blend LA2140e/Laropal® A 81 shows notable structural changes in FTIR when compared to the aged copolymer alone (Fig. 3a). An increase in absorption in the hydroxyl region between 3800 and 3000 cm^{-1} was observed (Fig. 8a). Upon aging, the two distinct carbonyl absorption bands at 1739 cm^{-1} and 1649 cm^{-1} from the unaged copolymer become difficult to detect. New absorption bands are formed and there is significant broadening within the region (Fig. 8b). Similar structural changes are observed when Laropal® A 81 is irradiated for 6 weeks (Fig. 6a and b). Therefore, it is likely that these notable structural changes observed by FTIR are due to the degradation of Laropal® A 81 rather than that of the base copolymer, LA2140e.

Changes in molecular weight distribution of the polymer blend were also observed by SEC. At 3 weeks of irradiation, SEC shows that the copolymer LA2140e (Fig. 9a) undergoes similar degradation when compared to aging of the copolymer LA2140e alone without the addition of the low molecular weight resin (Fig. 4). Shifts to shorter and longer retention times are observed and suggest polymer degradation via cross linking and chain scission, respectively. However, it appears that with the addition of Laropal® A 81, the copolymer LA2140e may degrade in a more aggressive fashion within the first 3 weeks of irradiation, as indicated by the large decrease in the polymer intensity peak at 7.8 min, as compared to Fig. 4. Despite these differences, with 6 weeks of irradiation, the polymer blend LA2140e/Laropal® A 81 has similar shifts in molecular weights as the copolymer alone.

Upon irradiation of the blend LA2140e/Laropal® A 81, Laropal® A 81 shifts to lower molecular weight when compared to the unaged resin. These results are comparable to the irradiation of Laropal® A 81 alone (Fig. 6c). This suggests that there is no influence of the base copolymer LA2140e on the degradation of Laropal® A 81.

In an effort to inhibit polymer degradation, the hindered amine light stabilizer Tinuvin® 292 was added to polymer blends at 2% (weight/weight) [17]. Hindered amine light stabilizers have been used to stabilize and inhibit the degradation of polymers by

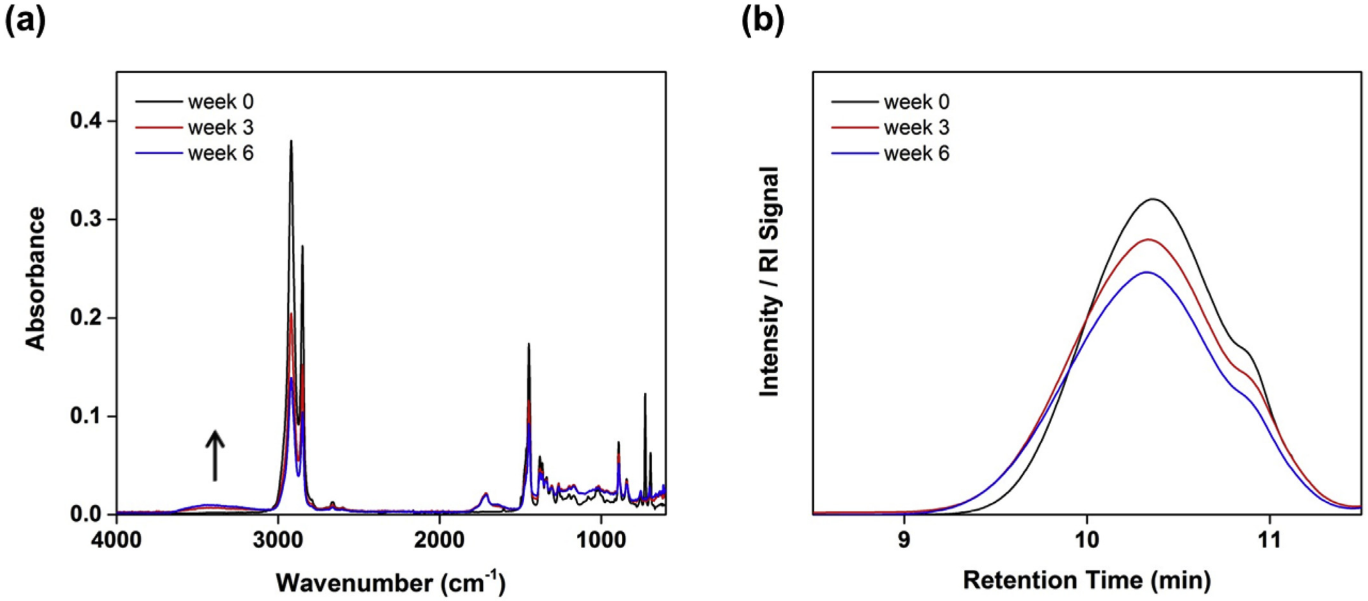

Fig. 7. (**a**) FTIR spectra from 4000 to 650 cm^{-1} of unaged (black), week 3 (red), and week 6 (blue) aged low molecular weight resin Regalrez® 1094. (**b**) SEC chromatograms of unaged and aged Regalrez® 1094. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

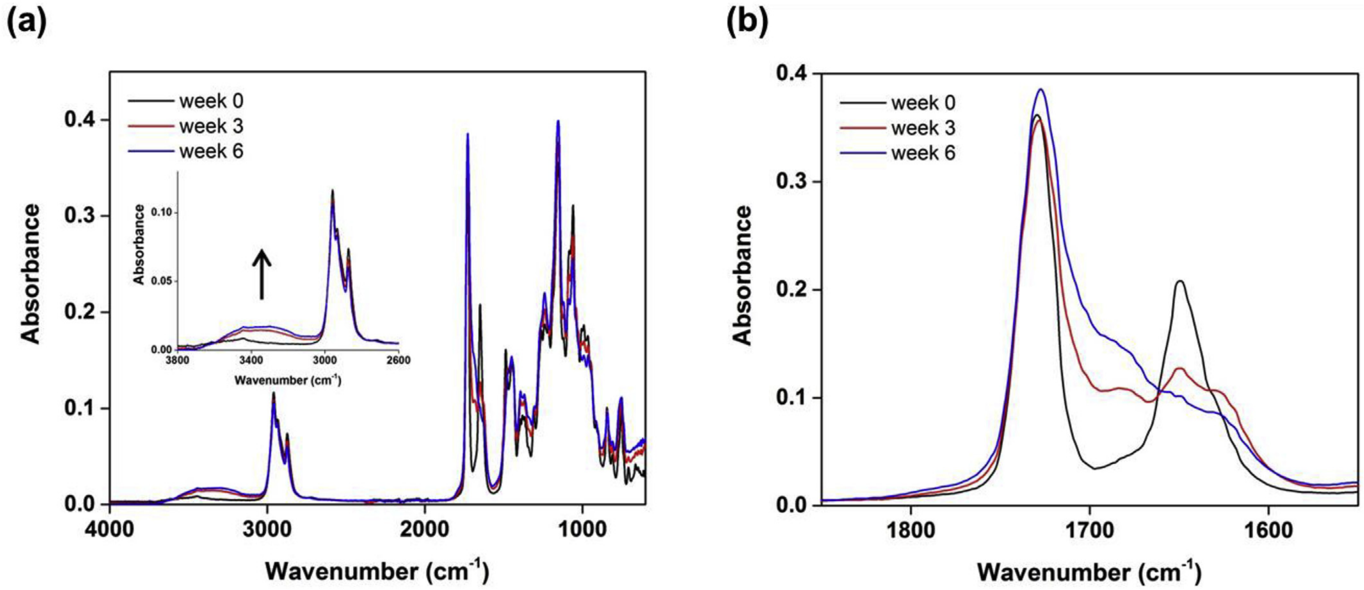

Fig. 8. FTIR of unaged (black), week 3 (red), and week 6 (blue) aged polymer blend LA2140e/Laropal® A 81. **(a)** FTIR spectra from 4000 to 650 cm^{-1} with inset of hydroxyl and C-H stretching region from 3800 to 2600 cm^{-1}. **(b)** FTIR spectra of the carbonyl region. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

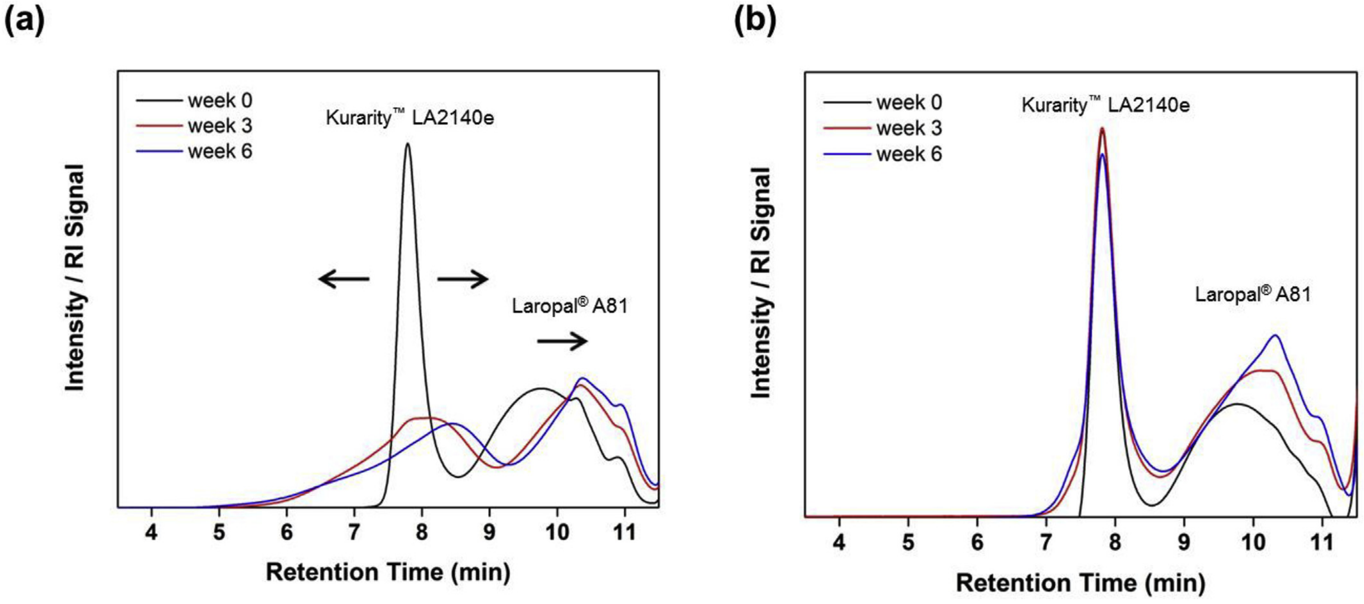

Fig. 9. **(a)** SEC chromatograms of unaged versus aged polymer blend LA2140e/Laropal® A 81. **(b)** SEC of LA2140e/Laropal® A 81 with the addition of Tinuvin® 292 (2 wt%).

continuously removing free radicals produced during photo-oxidation [31–33]. Several reports show the effectiveness of hindered amine light stabilizers as photo-degradation inhibitors for materials used within conservation [15,17,19]. Specifically, low molecular weight resins Laropal® A 81 and Regalrez® 1094 have been stabilized under simulated indoor conditions with the addition of Tinuvin® 292 [15,17]. Furthermore, Tinuvin® 292 has been shown to stabilize acrylic copolymers [34,35]. With the addition of Tinuvin® 292 it was observed by SEC that upon 6 weeks of irradiation the copolymer LA2140e becomes stabilized with minor changes to the molecular weight distribution relative to the unstabilized polymer blend (Fig. 9b). Laropal® A 81 still undergoes photo-degradation but exhibits less severe changes with the addition of Tinuvin® 292.

The changes in molecular weight averages for aged LA2140e and Laropal® A 81 with and without a hindered amine light stabilizer are reported in Tables 3 and 4. Although it is evident that photo-degradation occurs to the copolymer and low molecular weight resin, no changes in colour or opacity of the aged films were detected upon aging (Fig. 10). The unstabilized acrylic copolymer LA2140e exhibits a dramatic increase in the polymer dispersity index (PDI) suggesting a broad molecular weight distribution. However, with the addition of Tinuvin® 292, virtually no changes occur to the molecular weight averages of the copolymer after 6 weeks of aging, suggesting effective stabilization. Changes in molecular weight averages for Laropal® A 81 suggest that Tinuvin® 292

Table 3
Molecular weight averages of LA2140e during accelerated aging. Data gathered from blends containing LA2140e/Laropal® A 81 with and without Tinuvin® 292.

LA2140e	Irradiation (weeks)	M_n	M_w	PDI (M_w/M_n)
Unstabilized	0	58,000	66,000	1.1
	3	37,000	152,000	4.1
	6	27,000	220,000	8.2
+ Tinuvin 292® 2 wt%	0	62,000	67,000	1.1
	3	63,000	70,000	1.1
	6	53,000	66,000	1.2

Table 4
Molecular weight averages of Laropal® A 81 during accelerated aging. Data gathered from blends containing LA2140e/Laropal® A 81 with and without Tinuvin® 292.

Laropal® A 81	Irradiation (weeks)	M_n	M_w	PDI (M_w/M_n)
Unstabilized	0	1500	3900	2.6
	3	800	1700	2.1
	6	700	1400	2.0
+ Tinuvin 292® 2 wt%	0	1400	3200	2.3
	3	1200	2300	1.9
	6	900	2200	2.4

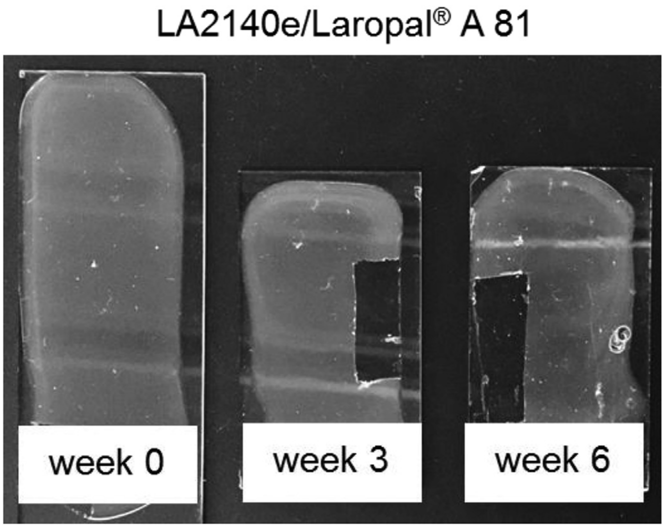

Fig. 10. Photographs taken with a black background of LA2140e/Laropal® A 81 dried films on microscope slides at week 0 (unaged), week 3, and week 6 aging. The contrast of the image was adjusted to help visualize the films. Areas where the film has been removed for analysis can be seen in the photographs.

provides some photo-stability when compared to the aged low molecular weight resin without a stabilizer.

Comparable results by FTIR and SEC were observed for the unaged and aged polymer blend containing the higher molecular weight copolymer, LA2330/Laropal® A 81. With the addition of Tinuvin® 292, the copolymer LA2330 exhibits minor photo-degradation (Fig. S4). Additionally, changes in molecular weight averages are reported in Tables S2 and S3.

3.3. Binary mixture of Kurarity™ 2140e and Regalrez® 1094

Upon irradiation of 6 weeks, the polymer blend LA2140e/Regalrez® 1094 shows some similar changes to that of the base copolymer LA2140e at 6 weeks of aging (Fig. 11a.) Observed by FTIR, there is a slight increase in the hydroxyl region upon aging, suggesting polymer or low molecular weight resin photo-oxidation. Additionally, with 3 weeks of irradiation there is an increase and broadening of the carbonyl absorption peak at 1727 cm^{-1} from the ester side groups on the base copolymer LA2140e. This increase in absorption is rather unexpected and cannot be explained.

However, with further irradiation of the polymer blend the carbonyl absorption peak decreases significantly when compared to the unaged blend (week 0 vs. week 6) (Fig. 11b). Additionally, irradiation of the polymer blend with the higher molecular weight acrylic copolymer LA2330 (Fig. S6) shows a decrease in absorption of the carbonyl peak upon aging at 6 weeks. These changes in absorption are not comparable to the aging behaviour of the copolymers LA2140e and LA2330 as observed in Fig. 3b and Fig. S2. In the aging experiments of the polymer alone, the carbonyl absorption band at 1727 cm^{-1} only exhibits a slight decrease in intensity. This suggests that there is another phenomena occurring in the polymer blends.

Upon aging, SEC shows that the Regalrez® 1094 within the blend has excellent stability with very minimal changes in molecular weight distribution upon irradiation (Fig. 12a). This is in full agreement with literature reports [16–18]. At 3 weeks of irradiation, the LA2140e copolymer within the polymer blend undergoes similar changes in molecular weight distribution as the aged copolymer alone, exhibiting both chain scission and cross-linking upon photo-degradation (Fig. 12a). However, it appears that with the addition of Regalrez® 1094, the rate of copolymer degradation is slower. This is observed by the remaining copolymer peak at 7.8 min in the SEC trace of week 6 (Fig. 12a). A comparison has been made between the SEC chromatograms of the copolymer LA2140e alone and the polymer blend, LA2140e/Regalrez® 1094 (Fig. 12b). At 6 weeks of irradiation it is clear from the residual copolymer peak at 7.8 min that Regalrez® 1094 reduces the degradation of LA2140e. Furthermore, changes in molecular weight of the copolymer LA2140e were gathered from the polymer blend and are reported in Table 5. This change in the rate of copolymer degradation may be explained by the possible interaction between the copolymer, LA2140e, and low molecular weight resin, Regalrez® 1094.

It has been reported that low molecular weight additives may migrate out of the adhesive bulk and concentrate at the surface [36,37]. Furthermore, it is known that non-polar additives are less miscible with polar acrylic copolymers resulting in a less homogenous mixture [36]. Upon drying, the film of LA2140e/Regalrez® 1094 (Fig. 13) is much more opaque than the dried film of the copolymer alone (Fig. 5) or the film of LA2140e/Laropal® A 81 (Fig. 10). This change in transparency suggests that phase separation occurs between the polar acrylic copolymer and the non-polar hydrogenated hydrocarbon resin. Furthermore, the surface of the polymer blend film is brittle and easily flakes during sample removal from the microscope slide. This polymer blend film surface is similar to the consistency of the dried film of Regalrez® 1094. It is not similar to the LA2140e copolymer film which is more flexible and not brittle. Although this is a qualitative observation, this further supports the phase separation and migration of Regalrez® 1094 to the surface.

Further evidence of phase separation and surface migration of Regalrez® 1094 is provided by the FTIR spectra in Fig. 11, where the carbonyl peak from the copolymer decreases significantly from 0 to 6 weeks. This drop in absorbance can be explained by migration of the low molecular weight resin to the surface, forming a layer of Regalrez® 1094. As ATR has a penetration depth of 0.5–3.0 μm, the layer of Regalrez® 1094 is not thick enough to prevent IR detection of some of the copolymer below the Regalrez® 1094 layer [38]. Variation in the carbonyl intensity over time may be due to increased phase separation of components. As a consequence of Regalrez® 1094 migrating to the surface of the dried film, the polymer blend film becomes opaque possibly scattering the light and reducing the irradiation to the LA2140e acrylic copolymer.

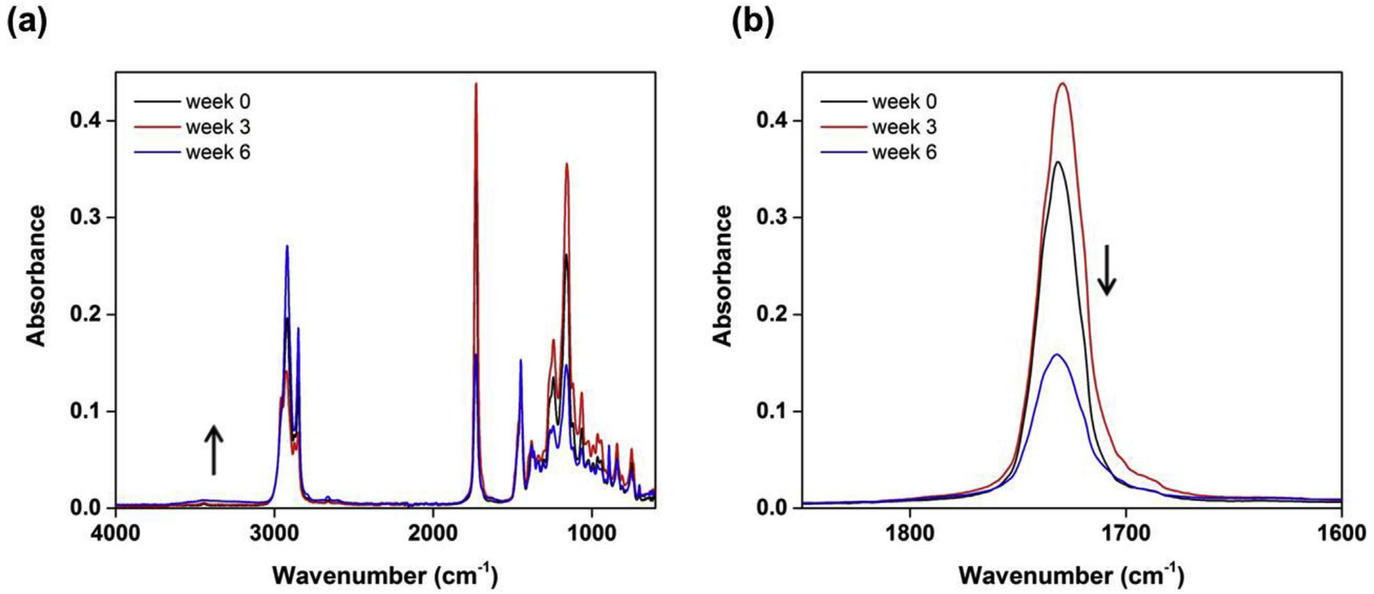

Fig. 11. FTIR of unaged (black), week 3 (red), and week 6 (blue) aged polymer blend LA2140e/Regalrez® 1094 **(a)** Full FTIR spectra from 4000 to 650 cm^{-1}. **(b)** FTIR spectra of the carbonyl peak at 1727 cm^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

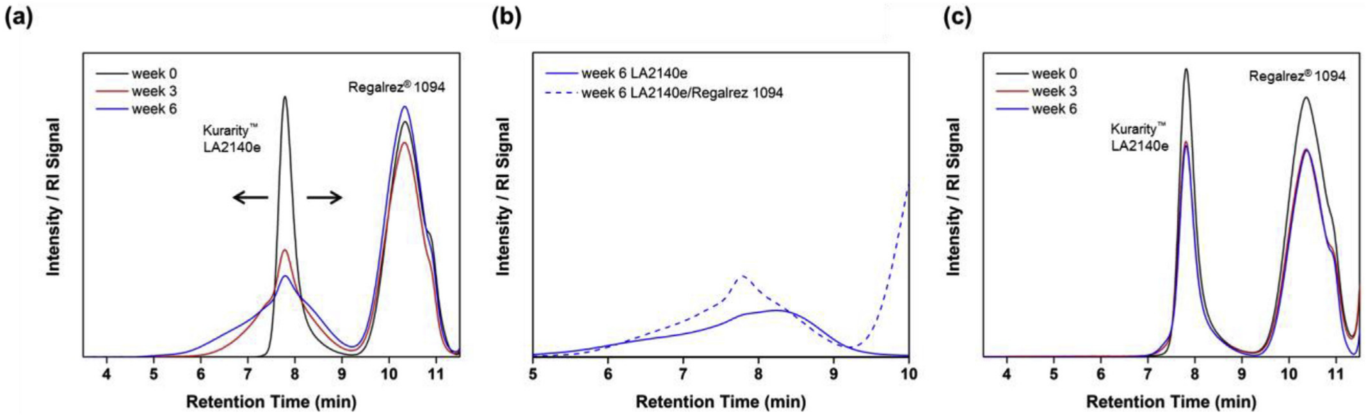

Fig. 12. **(a)** SEC chromatograms of unaged versus aged polymer blend LA2140e/Regalrez® 1094. **(b)** Comparison of LA2140e and LA2140e/Regalrez® 1094 SEC chromatograms at 6 weeks of irradiation. **(c)** SEC of LA2140e/Regalrez® 1094 with the addition of Tinuvin® 292 (2 wt%).

Table 5
Molecular weight averages of LA2140e during accelerated aging. Data gathered from blends containing LA2140e/Regalrez® 1093 with and without Tinuvin® 292.

LA2140e	Irradiation (weeks)	M_n	M_w	PDI (M_w/M_n)
Unstabilized	0	55,000	65,000	1.2
	3	51,000	121,000	2.4
	6	47,000	232,000	5.0
+ Tinuvin 292® 2 wt%	0	50,000	62,000	1.3
	3	50,000	65,000	1.3
	6	51,000	64,000	1.2

Tinuvin® 292 at 2% (weight/weight) was added to the polymer blend to investigate its efficacy in preventing polymer degradation. It was observed that with 6 weeks of irradiation the polymer blend LA2140e/Regalrez® 1094 becomes stabilized with no observable changes in molecular weight distribution (Fig. 12c). It is interesting to note that Tinuvin® 292 is even more effective in stabilizing the copolymer LA2140e in this polymer blend with Regalrez® 1094 than that of LA2140e/Laropal® A 81. As expected, a comparable trend in FTIR and SEC was observed for the polymer blend with LA2330/Regalrez® 1094 with and without stabilizer (Fig. S6).

Molecular weight averages for Regalrez® 1094 with and without Tinuvin® 292 were measured (Table 6). Unstabilized, aged Regalrez® 1094 shows minimal changes in molecular weight averages. Addition of the hindered amine light stabilizer fully protects the polymer from degradation, as seen in the molecular weight distribution. This inhibition was not unexpected, as previous studies report the efficacy of Tinuvin® 292 as a stabilizer for Regalrez® 1094 [17,18]. Comparable results are reported in Table S4 for Regalrez® 1094 when blended with LA2330.

3.4. T-peel strength of polymer blends

In order to investigate the potential use as consolidating adhesives, the peel strength of the polymer blends were studied. During consolidation an adhesive is placed between paint flakes or within paint cracks. Therefore, we have measured the strength of our materials when bonded between two flexible painted substrates. A fast drying alkyd oil paint (Winsor & Newton Griffin Lemon Yellow Alkyd Oil) was chosen to represent a modern painting.

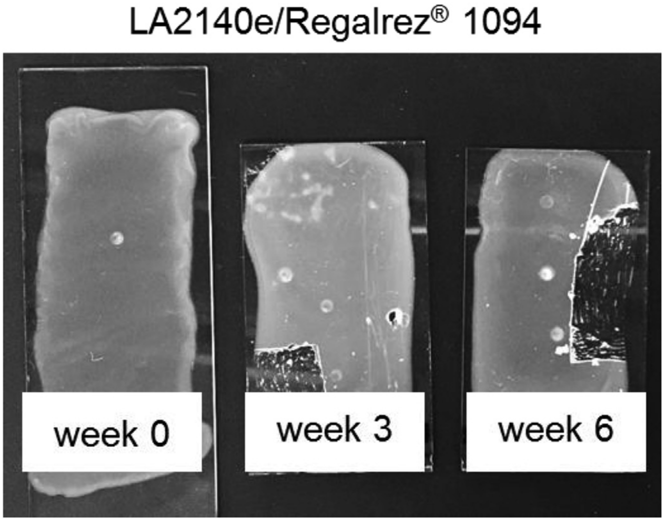

Fig. 13. Photographs taken with a black background of LA2140e/Regalrez® 1094 dried films on microscope slides at week 0 (unaged), week 3, and week 6 aging. The contrast of the image was adjusted to help visualize the films. Areas where the film has been removed for analysis can be seen in the photographs.

Table 6
Molecular weight averages of Regalrez® 1094 during accelerated aging. Data gathered from blends containing LA2140e/Regalrez® 1094 with and without Tinuvin® 292.

Regalrez® 1094	Irradiation (weeks)	M_n	M_w	PDI (M_w/M_n)
Unstabilized	0	800	1200	1.5
	3	900	1300	1.4
	6	900	1300	1.4
+ Tinuvin 292® 2 wt%	0	800	1100	1.4
	3	800	1100	1.4
	6	800	1100	1.4

Peel strengths of LA2140e alone and blends with low molecular weight resins Laropal® A 81 and Regalrez® 1094 are reported in Table 7. To gauge the performance of the polymer blends the peel strength of a commercial material often used as a consolidant, Paraloid™ B-72, was also measured. Comprised of ethyl methacrylate and methyl acrylate [39], this copolymer was chosen due to its popularity within the field, its excellent photo-stability [5,40], and its similar chemical composition to the Kurarity™ copolymers.

Data in Table 7 show similar peel strengths for all discussed materials including Paraloid™ B-72, which was used as a reference. At a ratio of 1:1 by weight, the addition of low molecular weight resins have a limited effect on the peel strength of the acrylic copolymer blend. This suggests, that phase separation between LA2140e and Regalrez® 1094 has a minimal effect on the overall peel strength of this blend. However, it is challenging to determine the degree of phase separation in the polymer blend between the two substrates in the peel test. Changing the drying environment of the polymer blend from open air to between two substrates may cause changes in the overall degree of heterogeneity in the sample. Regardless, these polymer blends show promise for use as consolidating adhesives for flaking paint as they exhibit similar peel strength to Paraloid™ B-72.

Table 7
Average initial T-peel strength at a sample width of 25 mm at room temperature of LA2140e, LA2140e polymer blends, and Paraloid™ B-72.

Adhesive	Peel Strength (N/mm)
LA2140e	0.09 ± 0.01
LA2140e/Laropal® A 81[a]	0.1 ± 0.01
LA2140e/Regalrez® 1094[a]	0.08 ± 0.01
Paraloid™ B-72 (commercial)	0.1 ± 0.04

[a] Blends were prepared at 1:1 ratio by dry weight of copolymer to dry weight of low molecular weight resin.

3.5. General discussion

The photo-degradation of acrylic copolymers Kurarity™ LA2140e and LA2330 was investigated by accelerated aging under simulated indoor conditions. Results show that upon irradiation the acrylic copolymers LA2140e and LA2330 undergo photo-degradation. Observed by SEC, degradation occurs via cross-linking and chain scission degradation, whereby the molecular weight distribution of the polymers broadens and shifts to shorter and longer retention times, respectively.

The rate of photo-degradation of the acrylic copolymers, according to SEC, is affected by the addition of a low molecular weight resin. When blended with Laropal® A 81, acrylic copolymer degradation occurs faster at week 3 when compared to aging of the copolymers alone. Contrary, when acrylic copolymers were blended with Regalrez® 1094, the acrylic copolymers exhibit slightly slower degradation even after 6 weeks of aging. These observations can be explained by the interaction between the acrylic copolymers and the low molecular weight resins.

It is reported that in a multicomponent system containing polymeric material and low molecular weight additives, the low molecular weight additives may migrate to the surface [36,37]. When combined with the polar acrylic copolymers, the non-polar Regalrez® 1094 blend dries to form an opaque film. This opacity suggests that the components have phase separated upon drying possibly due to the migration of the low molecular weight resin, Regalrez® 1094, to the surface. This is supported with examples in the literature, FTIR analysis of the surface, and by qualitative observations of samples. The film opacity may cause light scattering and reduced irradiation to the sub-surface layer of acrylic copolymer, slowing degradation.

To determine if the reduction in acrylic copolymer degradation within the acrylic copolymer/Regalrez® 1094 blend was the result of light adsorption, as opposed to light scattering, at the surface layer of Regalrez® 1094, UV–Vis measurements of Regalrez® 1094 in a THF solution were undertaken. The resulting spectrum, Fig. S7, shows minor absorption bands similar to those found in styrene and ethylbenzene in the 240–280 nm range [41], however at very low concentration. As Regalrez® 1094 is produced from the hydrogenation of short styrenic-like oligomer chains, it may be possible that the Regalrez® 1094 may not have been fully hydrogenated, leaving aromatic units. If this is the case, this means that the aromatic units in Regalrez® 1094 could reduce acrylic copolymer degradation by absorbing some irradiation and reducing the amount of light able to reach the acrylic copolymer. However, this seems very unlikely as the absorption bands in Fig. S7 and the FTIR spectra in Fig. 11a do not show a high concentration of aromatic species. This further suggests that light scattering is the dominant cause for the reduced acrylic copolymer degradation in blends containing Regalrez® 1094.

It is important to note that these results were obtained in a simulated indoor environment of daylight passing through window glass. Therefore, degradation of the polymer blends may be more severe in an outdoor environment where UV radiation far below 320 nm is present. However, according to our results, the addition of a hindered amine light stabilizer effectively inhibits the degradation for the acrylic copolymers within the blends (Table 8). To attain the highest stability, it is recommended to incorporate a hindered amine light stabilizer into the copolymer blends, especially if used in an outdoor environment.

Table 8
Summary of photo-degradation of copolymers and polymer blends with and without a hindered amine light stabilizer after week 6 of accelerated aging.

Adhesive	Unstabilized	+ Tinuvin® 292 (2 wt%)
LA2140e	Degrade	N/A
LA2140e/Laropal® A 81	Degrade/Degrade	Stable/Partially stabilized
LA2140e/Regalrez® 1094	Degrade/Stable	Stable/Stable
LA2330	Degrade	N/A
LA2330/Laropal® A 81	Degrade/Degrade	Stable/Partially stabilized
LA2330/Regalrez® 1094	Degrade/Stable	Stable/Stable

N/A = not applicable; accelerated aging of copolymers alone with Tinuvin® 292 were not studied.

4. Conclusions

This work aimed to investigate the photo-stability of commercially available acrylic tri-block copolymers blended with low molecular weight resins for their potential use as consolidating adhesives for the conservation of cultural objects. Results show that upon accelerated aging in simulated indoor conditions, the copolymer LA2140e undergoes cross-linking and chain scission degradation. Similar degradation mechanisms occur when the higher molecular weight copolymer LA2330 was irradiated under the same conditions. However, when blended with a low molecular weight resin the rate of copolymer degradation is affected. According to SEC, the blend with Laropal® A 81 degrades faster at week 3 than the copolymer by itself, whereas the blend with Regalrez® 1094 exhibits slightly slower degradation even after 6 weeks of aging. The influence on the degradation rate by the Regalrez® 1094 resin may result from phase separation and migration of the low molecular weight resin to the surface, thus reducing copolymer degradation by light scattering.

Although the copolymers exhibit photo-degradation under accelerated aging conditions, photo-degradation can be inhibited with the addition of a hindered amine light stabilizer. Copolymer blends with Regalrez® 1094 show the best photo-stability and with the addition of Tinuvin® 292 may be the most suitable to investigate further. Furthermore, peel strengths of polymer blends with Laropal® A 81 and Regalrez® 1094 are similar to that of the popular commercial material that is often used as a consolidant, Paraloid™ B-72. Consequently, these polymer blends show promise for the field of cultural heritage as consolidating adhesives for flaking paint. Future work focuses on formulating these binary polymeric blends specifically tuned for the consolidation of paint layers with applications including adhering flaked and cracked paint and consolidating powdery under bound paint.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymdegradstab.2018.11.010.

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