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ACCELERATED THERMAL AGEING OF ACRYLIC COPOLYMERS, CYCLOHEXANONE-BASED AND UREA-ALDEHYDE RESINS USED IN PAINTINGS CONSERVATION

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ABSTRACT

The monitoring of performance characteristics of resins was always an issue for the conservation community, since the stability of the art objects depends on the service life of conservation materials used. Among the resins commonly applied in the field of paintings conservation, four of the most popular ones, Paraloid B72, Primal AC33 (acrylic polymers), Ketone Resin N (cyclohexanone) and Laropal A81 (urea-aldehyde) were selected to be comparatively studied under accelerated ageing conditions. These resins have been used by the art conservators either as consolidant materials of the paint or as protecting varnishes for the painting surface.

The behaviour of the coatings under thermal ageing was investigated following a methodology depositing films of all materials onto different solid substrates (silicon wafers, quartz and simple glass slides) depending on the method of analysis used. Accelerated thermal ageing tests were conducted at 100 °C, for up to 432 hours. The morphological characteristics of the resins films (crack formations and surface alterations, coherence of film layers, thickness and surface roughness) were examined through scanning electron microscopy (SEM). Chemical changes of the resins were studied with FTIR and UV-Vis spectroscopy, while colour properties and thermal-chemical stability were also studied with spectro-colorimetry.

It was found that, although all four displayed changes concerning their colour and film thickness, the two acrylic polymers and the aldehyde resin exhibit high stability against chemical degradation compared to the cyclohexanone based resin. Complementary solubility and swelling testing were also applied and significantly aided in supporting the spectroscopy observations. Finally, microscopic examination of most resin films revealed cracking features which may sometimes render them unsuitable for application under uncontrollable conditions.

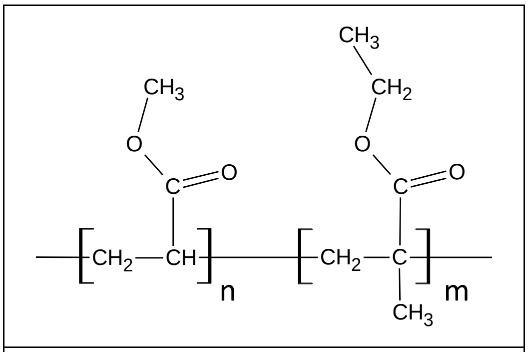
KEYWORDS: conservation, polymers, resins, thermal degradation, chemical stability.

1. INTRODUCTION

During the 1930s, synthetic resins were introduced in conservation, providing good optical properties (e.g. high refractive index and low molecular weight) comparable to the natural resins, but offering superior resistance to degradation.

One of the primary polymers which has been used for more than 50 years in paintings conservation is Paraloid B72, produced by Rohm & Haas and indicated as a methyl acrylate / ethyl methacrylate (MA/EMA, 30/70 %w/w) copolymer (Table I) (Bracci et al., 2003; Horie, 1995) with its composition slightly varying over time (De Witte et al., 1987). Today this resin is marketed in Europe and in USA as Paraloid B72 but in US the former name was Acryloid B72 (Lazzari et al., 2000). Over the years it has been used as a consolidant and varnish on a wide range of archaeological materials and art objects.

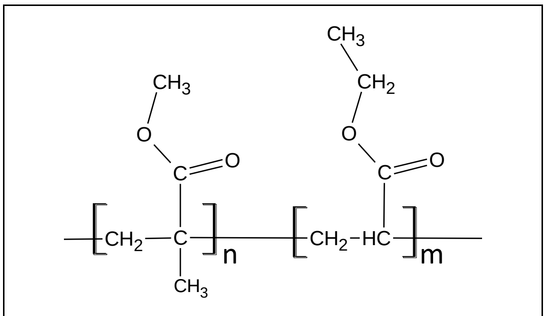
Table I. Paraloid B72



MA (30%) EMA (70%)

Primal AC33 is the European trade name of the polymer produced by Rohm & Haas, marketed as Rhoplex AC33in USA, with composition of ethyl acrylate/methyl methacrylate copolymer (EA/MMA, 60/40 %w/w) in water dispersion (Table II) (Horie, 1995). Primal AC33 has been applied as a consolidant material for all type of painted surfaces, stone surfaces, mortars and mural paintings. Primal AC33 has been discontinued and Rhoplex B-60-A has been suggested as a replacement.

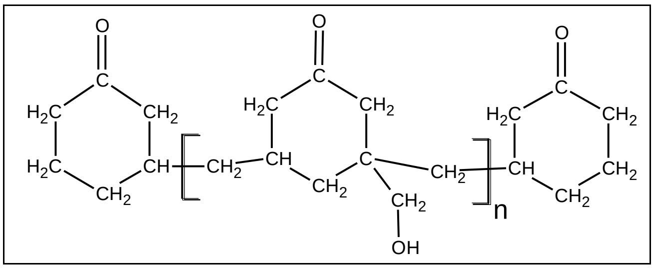
Table II. Primal AC33



MMA (40%) EA (60%)

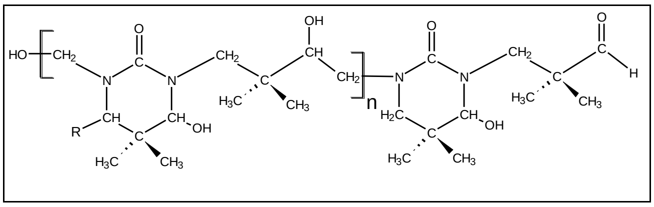
Ketone Resin N (cyclohexanone), produced by BASF, it is a low molecular weight oligomer of cyclohexanone including carbonyl, ether and hydroxyl groups (Table III) (Carbó et al., 2008). Ketone Resin N has been utilized by artists and conservators as varnish on easel and panel paintings, giving excellent properties as a film product, very similar to dammar. In the 80s the trade name was changed to Laropal K 80, but with the same chemical composition; today, however, the resin is out of production (De la Rie et al., 1989).

Table III. Ketone Resin N (according De la Rie et. al. 1989)



Laropal A81 (urea-aldehyde), produced by BASF, has been introduced to the conservation science thelate 90s and it has replaced Ketone Resin N. It's a low molecular weight resin with chemical composition of urea-aldehyde, formed through a condensation reaction between urea, formaldehyde and aliphatic aldehyde (isobutyraldehyde) (Table IV) (De la Rie et al., 1990; Reddington, 2015; Bonauce et al., 2013). Laropal A81 is mainly used as varnish on easel paintings and panel paintings, with excellent optical properties very similar to traditional varnishes.

Table IV. Laropal A81 (according Zhang et al. 2009 and Bonaduce et al. 2013)



The above resins have been for decades the main products used by conservators for the needs of restoration and stabilization of the antiquities and art objects (De la Rie, 1989; Robson, 1992). These resins are applied on the painted surface of the art work; either for securing paints stability on the role of a consolidant; or as varnish for protecting the painting surface and for improving the appearance of a painting, by increasing the chromatic ability of both colour gamut and contrast. The painting surface is been composed from the pigment particles mixed together with a binding material (such as oil, egg tempera etc.).

Natural ageing of materials used for conservation purposes may affect in general their original macroscopic properties as a result of the alteration of optical properties (e.g. loss of transparency and changes in colour), blooming, brittleness and changes in solubility, due mainly to chemical alterations including cross-linking (McNeill, 1992; Johnson et al., 1996). Therefore, the long-lasting stability of certain resins in terms of optical and physical characteristics is of great interest to conservators and is closely related to their chemical stability. Moreover, various resins can be found on the original works of art as overlapping layers, for example Paraloid B72 is been applied over Ketone Resin N for securing longer stability of cyclohexanone resins.

In the above context, focus is needed on the degradation processes and the evaluation of the life service of these materials when they are used in the conservation of museum objects. In this paper, the results of investigation of the stability of the resins during thermal accelerated ageing, using colorimetry, molecular spectroscopy (UV-visible absorbance and FTIR) and differential scanning calorimetry, aided by swelling testing, solubility and contact angle measurements, are presented. This was achieved by applying relatively high temperatures taking into account that three of the above products (Paraloid B72, Primal AC33 and Ketone Resin N) have been used extensively in conservation since 1950.

This experimental work is part of a broader study on degradation processes of Paraloid B72, Ketone Resin N, Primal AC 33 and Laropal A81 under various accelerating ageing conditions (thermal, photochemical and high humidity levels). Results on the thermal ageing stability of standardized samples in the form of films under laboratory thermal ageing are presented and discussed here. The findings of the present work can serve as a baseline towards the estimation of the behaviour of these products as a function of their application time under variable environmental museum conditions.

2. EXPERIMENTAL

Methods of film preparation and thermal ageing

The resin test specimens were studied in the form of thin films, prepared by spin coating of 10% (w/w) tetrahydrofuran (THF) solutions of Paraloid B72, Ketone Resin N and Laropal A81, as well as 30% (w/w) in distilled water solutions in the case of Primal AC33 on silicon wafers at 3000 rpm for 120 sec (Headway Research INC model No CR15). All films were subsequently left for 24 h to set. Concentrations of materials solutions and spin coating conditions were chosen in order to achieve films of uniform thicknesses, less than 1 μm. The above prepared films were accordingly analysed by FTIR spectroscopy. Similar films were prepared through spin coating on quartz slides, which were used for UV-Vis absorption. For SEM analysis, colorimetry measurements and solubility tests, a similar film series of all materials were prepared through air/hair brushing on glass slides. Finally, for swelling tests and DSC analysis, the corresponding films were produced after solvent evaporation from resin solutions (after 5 months curing).

Film thickness were determined with a XP2 AMBIO micro-profilometer, and ranged between 460 and 920 nm. Consequently, accelerated thermal ageing of the specimens was carried out in a laboratory oven, at 100 ± 2 °C, for 432 hours (Favaro et al. 2006; Lazzari et al., 2000; Carbó et al., 2008).

Methods of analysis

Fourier transform infrared (FTIR) spectroscopy

FTIR was used, first for providing detailed information on the resins' chemical structure and secondly, for observing changes in chemical bonding during accelerated ageing, allowing for evaluations of their conditions (Cavicchioli et al., 2006).

Spectra were collected on a Bruker-Tensor 27 spectrometer, in transmission mode, in the range of 4000-400 cm^{-1} (resolution 4 cm^{-1}) (Derrick et al., 1999). Due to the relatively low film thicknesses (<923 nm) which were cast either on silicon wafers or quartz plates, oxygen diffused throughout the material allowing for efficient oxidation rates (Feller et al., 1971). Transmission mode allowed collection of average information across films, representing changes in the entire body of each material. Additionally, care was exerted so that all measurements were carried out at the same spot within the same specimen, so that the results can be comparable.

FTIR spectra were processed on Bruker OPUS software, version 4.2; baseline correction was applied with special care not to affect any particular absorption. No smoothing or normalization was applied.

Colorimetry

Since colour changes strongly depend on the degradation of resins (Favaro et al., 2006), the determination of the colour properties during thermal ageing of the resins was used as an indicator for their preservation during thermal ageing. Colour parameters were measured with a Minolta CM-2002 portable reflectance spectrophotometer, including a xenon lamp and UV radiation cutting filter and an integrating sphere which allows diffuse reflectance measurements on the samples' surface, with spot size 4mm. The results were reported in CIE 1976 L*a*b* system (Iňigo et al., 1997). This system is designed to approximate human vision (perception of colour) while enabling the determination of colour numerically. The L* value refers to lightness variable, while a*, b* the green-red and yellow-blue coordinates respectively (García-Talegon et al., 1998). The colour difference between different stages was calculated according to the equation below (Robertson, 1977; Valleri et al., 1997):

$\Delta Eab^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{½}$.

Presentation of the colorimetry measurements are presented in chromatic diagrams from -20 to 20 in CIE 1976 L*a*b* system,.

UV-Visible (UV-Vis) spectroscopy

UV-Vis spectroscopy was used in order to detect the formation of chromophore groups during the thermal ageing of resins (Carbó, 2008; Campbell et al., 1994). The UV-Vis spectra were collected using a Perkin-Elmer UV-Vis Lambda 40 spectrophotometer, at wavelength range 1100-190 nm.

Scanning Electron Microscopy (SEM)

Microstructure and texture of the resins films before and after thermal ageing were examined in SEM (FEI – Quanta Inspect), coupled with an energy dispersive X-ray spectrometer (EDS). Aiming to eliminate the damage of the films by the electrons beam (Campbell et al., 1994), the specimens were coated with gold.

SEM examination was mainly performed for the morphological examination of resins in initial state, since materials' thermoplastic ability produce reshaping of the resin when is exposed above its Tg temperature.

Differential Scanning Calorimetry (DSC)

The thermal behaviour of resins was examined through DSC by determining the glass transition temperatures (Tg) of materials. DSC measurements were carried out with 2920 Modulated Differential Scanning Calorimetry (TA Instruments). Sealed aluminium pans containing samples (10-13 mg) detached from films were heated under nitrogen atmosphere from 0-220 °C with scanning rate 5°C/min (D'Orazio et al., 2001).

Swelling and Solubility tests

Aiming to study the effect of thermal ageing on the solubility and therefore, the reversibility of the resins, swelling and solubility tests were carried out (Cocca et al., 2004). For the swelling test, films of each resin were weighed (approximately 0.5 gr) and immersed in different solvents for 24 hours (5 ml of each solvent). After 24 hours the excess solvents were decanted off and the samples were left to dry for 48 hours. The dried samples were weighed and the percentage of swelling was calculated by the following equation (Duffy, 1989): $\frac{W_2 - W_1}{W_1} x100$

where, W_1= the weight of the sample before the addition of solvent, W_2= the weight of the sample after drying for 48h.

For the solubility test, different types of solvents were tested according to the method proposed by Feller (Feller et al., 1971). The solvents were composed of mixtures of cyclohexane, toluene and acetone, providing a series of solvents of increasing polarity. For each resin, the dispersion force contribution (f_d), the dipolar contribution (f_p) and the hydrogen bonding (f_h) parameters were determined and the solubility ability was evaluated based on Teas triangular diagram (Feller, 1978). The given solvents were applied by using cotton swab; when the resins were removed in less than a minute by normal rubbing, each resin was accordingly categorized as soluble or not soluble in this solvent mixture (Yang et al., 2004)..

Contact angle measurements

Contact angle measurements provide one of the most rapid methods for determining surface alteration on resin films (Ploeger et al., 2009). Optical contact angle were performed using Contact Angle Model EWS DIGIDROP GBX instrument equipped with high speed camera, monitored with time step, 21 frames per second. To investigate the changes in surface energy, the method was performed on samples before and after accelerating ageing.

3. RESULTS AND DISCUSSION

Resin casting conditions allowed for the preparation of films similar to those used on art objects, which are typically applied with the use of hairbrush and airbrush. The microstructure and chemical parameters of the resins were studied during thermal ageing at preset time periods, while the results were compared to those of the reference specimens (not aged). The above ageing procedure was applied for studying the degradation mechanisms of the four resins and for comparing their durability. The chosen temperature, well above the Tg values of all materials, allowed significant acceleration of ageing procedures. In addition, these resins have been used as consolidation materials in conservation practise; as such, heat is often applied, reaching temperatures well above their Tg values, thus activating the thermoplastic ability of the materials (Young, 2012). Therefore, ageing temperature (100 °C) was chosen, well above the highest Tg value (85 °C) of the examined resins.

The results are divided in four sections corresponding to the four resins examined, for each of which physicochemical change occurred during thermal accelerated ageing is been shown along with the characteristic spectra.

Paraloid B72

Examination of an air brushed film on glass slide before ageing revealed that its adhesion to the substrate was very good. However, at high magnification (x100000) an extended cracking of the film was recorded (Figure 1) whereas insoluble material was on the film surface which resulted from the air brushing application (Figure 2).

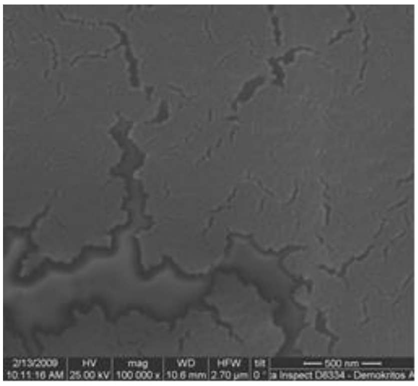


Figure 1. SEM micrographs in the initial state; resin is coated by air brush on glass slide showing cracking of the resins

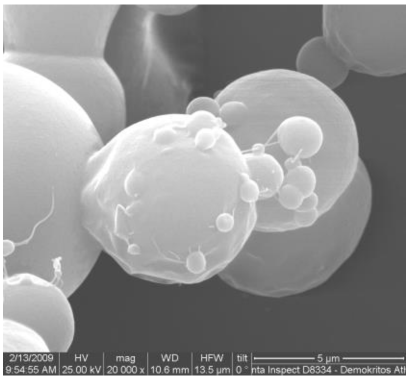


Figure 2. Paraloid B72, spherical aggregates material on the film surface produced during air brushing application.

Observation of film cross sections exhibited two layers. Closer examination of the cross section showed good cohesion among the layers (Figure 3). EDS analysis identified the presence of TiO_2 in concentrations up to 3%, as also reported in the product's certificate (Rohm & Haas). TiO_2 pigments are usually added to certain polymeric materials in order to absorb light energy and protect them from photochemical and thermal degradation reactions (usually oxidations of the polymers) (Yang et al., 2004; Spathis et al., 2004).

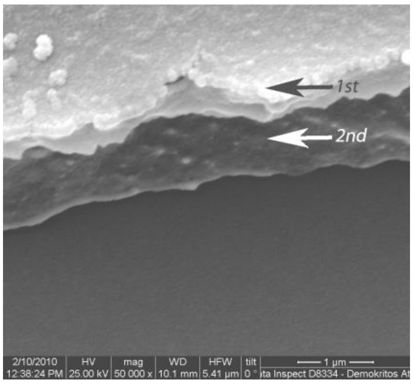


Figure 3. SEM micrographs of Paraloid B72, film cross section revealing polymer's layers.

Thicknesses of films were measured before and after ageing by micro-profilometry and compared with the values obtained after SEM examination. The film thickness after thermal ageing was found to be reduced by 14 % due to solvent removal and subsequent decrease of the film free-volume (Table V). Nevertheless, the heating above Tg temperature resulted the re-shaping of the film, since at temperatures above Tg thermoplastic materials behave as flowing liquids (Horie, 1995). As a result, after solidification SEM examination revealed that the network of micro-cracks had been reduced (Figure 4), while the spherical air-brushing formations have been disappeared.

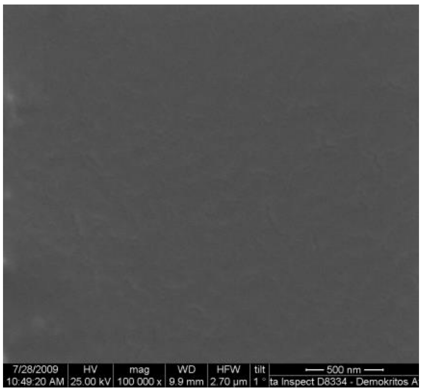


Figure 4. SEM micrographs after ageing; showing micro-cracking of the resins

DSC analysis of Paraloid B72 film in its initial stage revealed a Tg temperature of 25 °C, while after thermal ageing this was found to be 42 °C (Table V); the Tg value is reported by the manufacturer at 40°C. The temperature increase after ageing of approx. 17°C can be attributed to solvent evaporation, which consequently produces a change in the polymer free volume; this can also be an evidence of first stage degradation affecting its physical properties.

After thermal treatment Paraloid B72 remained soluble in the more polar solvents mixture, although swelling and solubility tests after ageing unveiled 8.7% solubility reduction (Table V).

After thermal ageing a decrease 8% in the water-film surface contact angle was observed, indicating an increase in film surface hydrophilicity and change of surface polarity (Table V).

Testing of this material after thermal ageing revealed the chemical stability of this product. Noticeable changes due to thermal ageing were related to colouration; although not perceptible to naked eye, they were evident through colorimetric measurements. More specifically, there was a significant change on b* (from 1.13 to 3.15 which, corresponds to a colour change of ΔE= 2.58) which indicates area yellowing effect.

Table V. Examination methods for investigating thermal stability of Paraloid B72

Thermal ageing – Paraloid B72			
Examination method	**Reference material**	**Aged**	**Notes**
Micro-profilometry Films formed by spin coating	923 nm	789 nm	Reduce thickness 14 %
Feller Test (solubility test) Films casted on glass slide	Cyclohexane 75 % Toluene 25 % Teas parameter (fd) N 91	Cyclohexane 25 % Toluene 75 % Teas parameter (fd) N 83	Reduce solubility 8.7 %
Swelling by weight loss (%) Films casted as membrane	Distilled water 4.08 Isopropanol 49.01 Toluene -6.05	Distilled water -0.68* Isopropanol 0.33 Toluene 0.68	* Negative values indicated dissolution of the membrane
Contact angle Films casted on glass slide	72	66	Decreased 8 %, as more hydrophilic
DSC Tg Films casted as membrane	Tg = 25 °C (0,1728 J/g/ ℃)	Tg = 42 °C (0,1931 J/g/ ℃)	Tg 40 ℃ as reported on Technical Datasheet

UV-Vis absorption spectroscopy did not show any significant changes after ageing at 100 °C for 288 hours. Nevertheless, after thermal treatment up to 432 hours the UV spectra of Paraloid B 72 exhibited a small increase in film scattering at λ>240nm, which may be correlated to the decrease of the film free-volume and subsequent increase of density as previously mentioned (Figure 5) (Lazzari et al., 2000; Miliani et al., 1991). The high stability of Paraloid B72 film upon thermal ageing at 100 °C was also supported by FTIR.

The infrared absorption spectra of Paraloid B72 at its initial state showed the following characteristic peaks: C–H stretching (2900-3000 cm^{-1}), ester carbonyl stretching at 1733 cm^{-1}, C–H bending at 1448 and 1388 cm^{-1}, and finally the multiple absorptions due to stretching of C–O ester bonds from 1238 to 1161 cm^{-1} (Ciantore et al., 1996). Peaks with assignments of infrared spectra recorded from Paraloid B72 at its initial state are shown in Table IX (see structure in Table I).

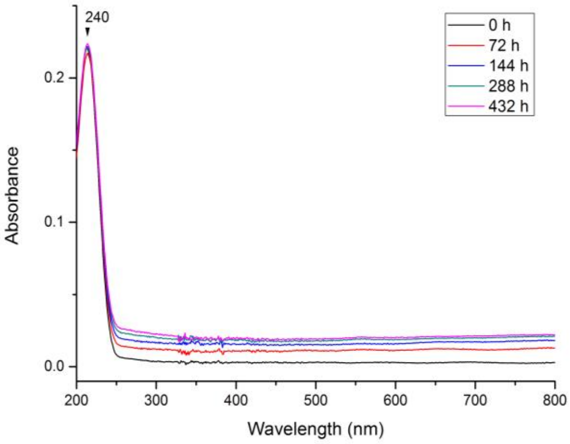


Figure 5. UV-Vis absorption spectra of Paraloid B72 10 % (w/w) in THF. During different times (0-432 hours) of thermal ageing at 100 °C

The infrared spectra of the resin remained almost unchanged throughout thermal ageing, with small decrease in absorption intensity of carbonyls recorded at the latest stages of ageing, indicating minor oxidative degradation of the material.

Primal AC33

SEM examination of the initial film on a glass slide revealed that it was very homogeneous and had good adhesion to substrate. On the film surface, insoluble material in the form of spherical aggregates, similarly to Paraloid B72 were evident, along with distinguished cubic crystals, indentified by EDS as NaCl (Figure 6). The presence of NaCl is probably attributed to the use of industrial water by the manufacturing company during the production of the aqueous dispersion consolidant.

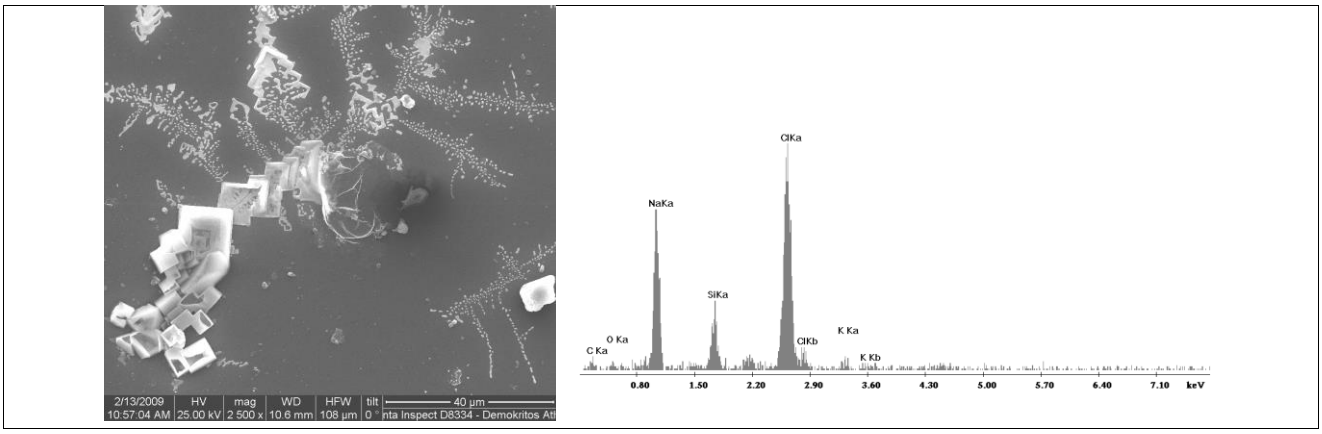
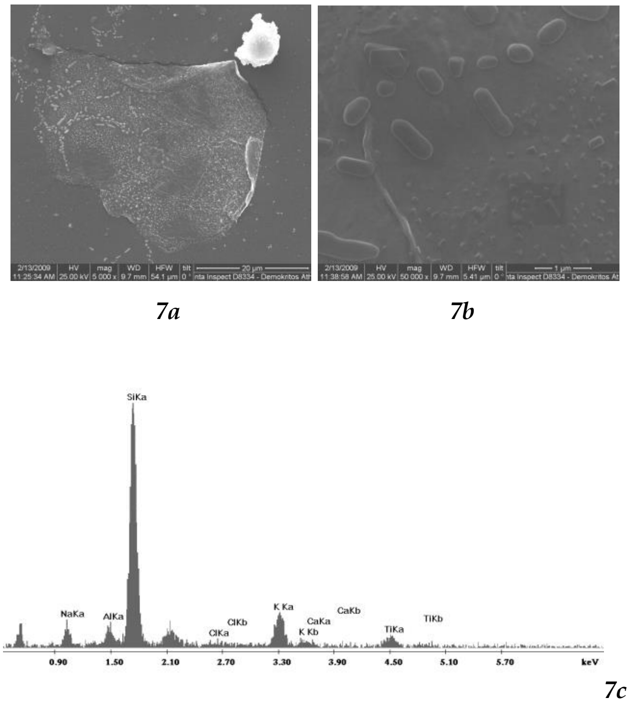


Figure 6. SEM micrographs of Primal AC33 films coated by hair brush on glass slide showing: NaCl salts on the film surface which was investigated by EDS analysis, Si peak is due to glass substrate



7a *7b*

7c

Figure 7. SEM micrographs of Primal AC33 films coated by hair brush on glass slide showing: 7a, 7b, particles with significant TiO_2 concentration which was investigated by EDS analysis, Si peak is due to glass substrate (figure 7c)

Thorough examination showed a group of particle formations with different shapes and sizes, such as long with rounded edges (1 μm size), small spherical (500 nm), small square and needle-shape (with a variety of sizes ranging from 50 nm to 500 nm). These particles contained TiO_2 in concentration up to 6,5 % confirming the use of this oxide as a stabilizer agent towards UV photocatalytic reactions. (Figure 7a,b,c).

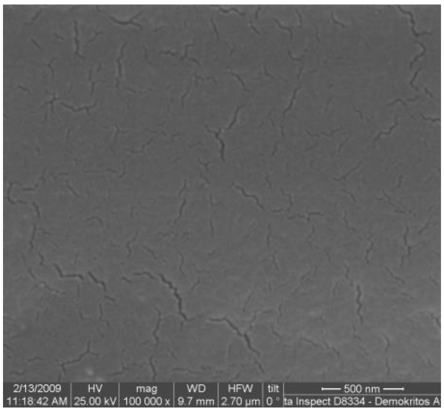


Figure 8. SEM micrographs in the initial state, of Primal AC33 film coated by air brush on glass slide substrate showing cracking of the resin

Similarly to Paraloid B72, a network of fine cracks was detectable at high magnification (X100000) (Figure 8). Thermal ageing resulted in the reduction of the cracking network, which was associated with the thermoplastic ability of the material, with simultaneous thickness reduction by 2 % (Table VI).

DSC analysis of Primal AC33 films in initial stage showed Tg transition at 62 °C, while after thermal ageing the value dropped to 22 °C (Table VI); the manufacturer's value is reported at 16 °C. The large difference of the Tg values of the polymer in its initial stage can be attributed to its water dispersion and subsequent hydrogen bonding and other secondary bonding which might have affected Tg. The

Tg value difference which was recorded after thermal ageing can be attributed to water evaporation.

Swelling and solubility tests of Primal AC33 showed 12 % reduction in solubility after thermal treatment (Table VI).

After thermal ageing, a 117 % increase in the water-film surface contact angle was observed, indicating an increase in film surface hydrophobicity and increased in film surface polarity (Table VI). The increased hydrophobicity can be justified on the basis of chemical changes induced to ester groups upon accelerated ageing, as seen in FTIR results below.

Colorimetric measurements of Primal AC33 indicate colour stability during the 144 hours thermal ageing, but showed increase of b* (from 1.92 to 3.26 which corresponds to colour difference of $\Delta E= 1.5$) after 432 hours thermal ageing. This finding indicates difference in yellow hue and suggests thermally induced structural chemical changes; this is supported by the UV-Vis and FTIR recordings (see below).

UV-Vis measurements were carried out at different ageing times and showed spectra with a characteristic intense peak centred at 214 nm and assigned to the C=O absorption. During ageing at 100 ˚C for 288 hours, an insignificant change, i.e. a minor decrease (from 0.24 to 0.22) of the ~214 nm absorption peak was observed (Figure 9). Beyond 432 hours of ageing the intensity of the 214 nm peak continue decreasing to 0.20.

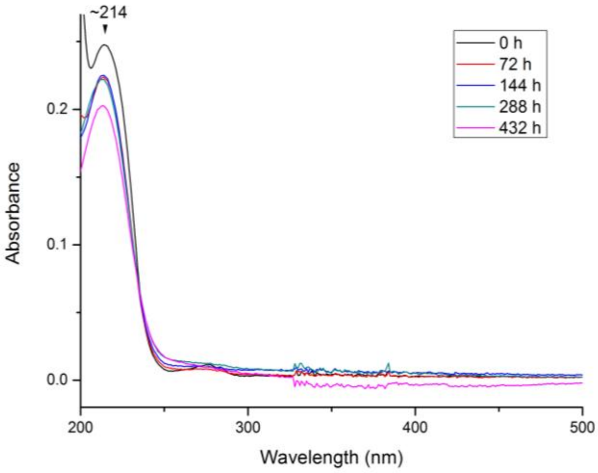


Figure 9. UV-Vis absorption spectra of Primal AC33 10 % (w/w) in distilled water. During different times (0-432 hours) of thermal ageing at 100 °C.

Table VI. Examination methods for investigating thermal stability of Primal AC33

Thermal ageing – PrimalAC33			
Examination method	**Reference material**	**Aged**	**Notes**
Micro-profilometry Films formed by spin coating	663 nm	649 nm	Reduce thickness 2 %
Feller Test (solubility test) Films casted on glass slide	Cyclohexane 75 % Toluene 25 % Teas parameter (fd) N 91	Toluene 100 % Teas parameter (fd) N 80	Reduce solubility 12 %
Swelling by weight loss (%) Films casted as membrane	Distilled water -10* Isopropanol 26.53 Toluene 7.17	Distilled water 0* Isopropanol 0.63 Toluene 1.31	* Negative values indicated dissolution of the membrane
Contact angle Films casted on glass slide	30	65	Increased 117 %, indicated as more hydrophobic
DSC Tg Films casted as membrane	Tg = 62 °C (0,1209 J/g/ ℃)	Tg = 22 °C (0,1470 J/g/ ℃)	Tg 16 ℃ as report on Technical Datasheet

Infrared spectra of Primal AC33 (see structure in Table II) are similar to Paraloid B72 with characteristic absorptions on the C–H region (2900-3000 cm^{-1}), carbonyl stretching at 1734cm^{-1}, C–H bending at 1448 and 1387 cm^{-1}, and multiple absorptions due to C–O stretching at 1238, a doublet at 1176 and 1161cm^{-1} (Cocca et al., 2004). Spectroscopic distinction between the two acrylic copolymers can be made on the basis of the 1238, 1176 and 1161 cm^{-1} peaks which are observed in the former. Specifically, the doublet at 1176/1161 cm^{-1} is typical of the copolymer with the higher weight percentage of the methyl acrylate component (i.e. Primal AC33), which is more intense than the doublet in Paraloid B72 (Chiantore et al., 1996) (Figure 9). Peaks with assignments of infrared spectra recorded from Primal AC33 film at its initial state are shown in Table IX.

Spectra collected from the film after various stages of ageing showed that it remained almost unchanged throughout 144 hours of thermal ageing, while a small decrease in intensity of the ester C=O at 1734 cm^{-1} was recorded after 288 hours ageing, as well as the ester links at 1238, 1176 and 1161 cm^{-1} which were further reduced until 432 h (Figure 10) (Miliani et al., 2002).

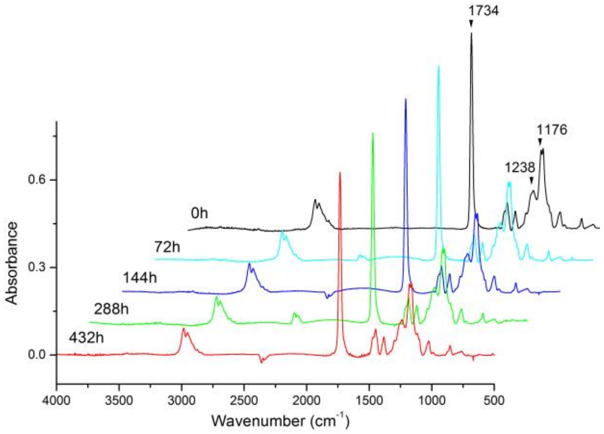


Figure 10. FTIR spectra of the Primal AC33 10 % (w/w) in distilled water. The polymer remained almost unchanged throughout 144h thermal ageing, a change of intensity recorded after 288 hours ageing

The above results suggest that Primal AC33, although an acrylic copolymer, known for thermal stability (Chiantore et al., 2001), is less stable than Paraloid B72. The presence of methyl acrylates in both structures, which as they have been reported that do not favour chain scission reactions, contribute for the stability of both materials (Bracci et al., 2003; Lazzari et al., 2000). In addition, the presence of methyl groups or hydrogen in the copolymer backbone, which exist in both structures (Table I, II) is another reason for their stability. However, the lower percentage (40 %) of the MMA unit in Primal AC33 as compared to 70 % of the EMA in Paraloid B72 is possibly responsible for the observed relative lower stability of the former.

Ketone Resin N

Morphological examination at high magnification (X100000) of the hair brushed resin on glass slide before ageing, revealed an extensive cracking of the film, whereas flaky aggregates material on the surface was also observed (Figure 11, 12).

After thermal ageing, the liquification of Ketone and the consequent transformation to the solid state result the complete disappearance of cracking, enhancing the beneficial thermoplastic effect that was first noted in the micro-morphology of acrylic resins. Nevertheless, the film thickness was reduced considerably to 27 % (Table VII). As in the case of Paraloid B72, EDS analysis indentified a significant TiO_2 concentration (up to 5 %), which, as already mentioned, was aimed to function as a UV blocking agent.

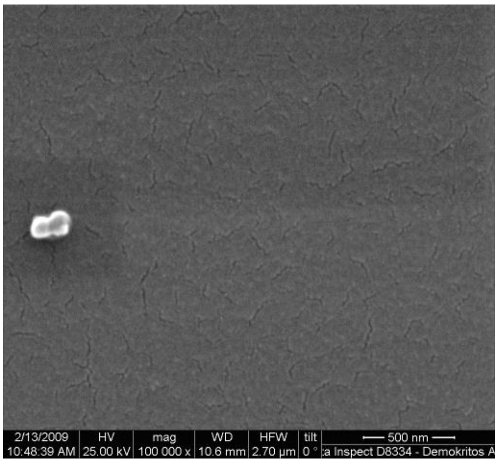


Figure 11. SEM micrographs in the initial state, of Ketone Resin N film coated by air brush on glass slide substrate showing cracking of the resins

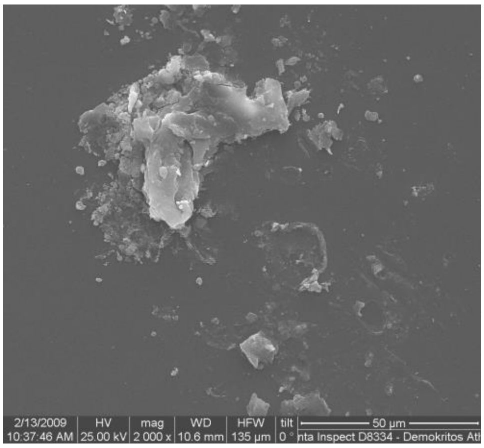


Figure 12. Ketone Resin N: flaky aggregates of material

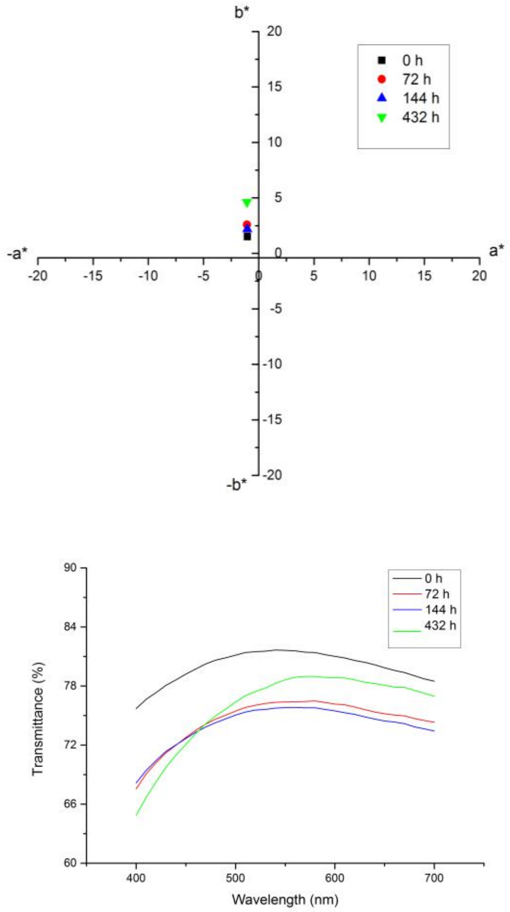
DSC analysis of the Ketone Resin N film sample in its initial state showed a Tg value at 33 °C, while after thermal ageing the Tg was found to be raised at 48 °C (Table VII); a Tg value of 75-85 °C is being reported by the manufacturer. The approximately 15°C change after thermal ageing can be attributed to solvent evaporation and possibly, beginning of degradation.

Swelling and solubility testing showed Ketone N resin presenting 15 % solubility decrease upon ageing (Table VII).

After thermal ageing a decrease of 88 % in the water-film surface contact angle was observed, indicating an increase in film surface hydrophilicity and increase of polarity. After thermal ageing, the resin exhibited intense swelling and penetration of the liquid into the film (Table VII).

Table VII. Examination methods for investigating thermal stability of Ketone Resin N

Thermal ageing – Ketone Resin N			
Examination method	**Reference material**	**Aged**	**Notes**
Micro-profilometry Films formed by spin coating	463 nm	338 nm	Reduce thickness 27 %
Feller Test (solubility test) Films casted on glass slide	Cyclohexane 100 % Teas parameter (fd) N 94	Toluene 100 % Teas parameter (fd) N 80	Reduce solubility 15 %
Swelling by weight loss (%) Films casted as membrane	Distilled water 18.75 Isopropanol 4.34 Toluene -7.60*	Distilled water -2.03* Isopropanol -2.03* Toluene 0.00	* Negative values indicated dissolution of the membrane
Contact angle Films casted on glass slide	80	10	Decreased 88 %, indicated as more hydrophilic
DSC Tg Films casted as membrane	Tg = 33 °C (0.2653 J/g/°C)	Tg = 48 °C (0.2420 J/g/℃)	Tg 75-85 ℃ as report on Technical Datasheet



13a

*Figure 13a,b. Colorimetric measurements La*b* during ageing of Ketone (a). Visible spectrum measurements (b)*

The colorimetric measurements indicate a gradual colour change with ageing, which at 432 hours, starts to be perceptible even by naked eye. In terms of actual values, there was a change of b* (from 1.52 to 4.63, ΔE= 3.16) indicating a shift towards yellow (Figure 13a,b).

UV-Vis spectra of the material in its initial state showed a characteristic absorption shoulder at ~270 nm. Thermal ageing (72hours) resulted in an absorption peak at ~270 nm which increased its intensity with ageing time (0.31 after 432 h; Figure 14); these observations are in accordance with the colorimetric observations (see above).

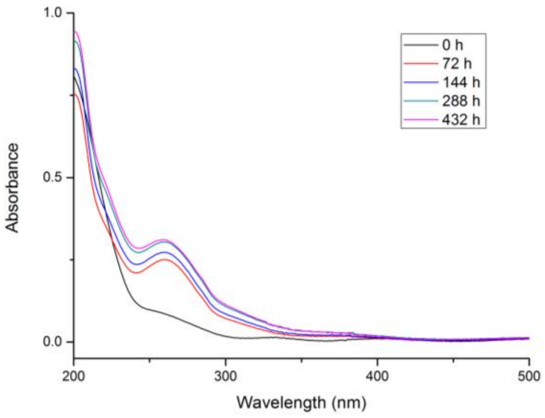


Figure 14. UV-Vis absorption spectra of Ketone

This behaviour of Ketone Resin N, along with its associated yellowing upon ageing, has been previously reported in the literature (Carbó et al., 2008). These changes can be attributed to the formation of small quantities of unsaturated species due to dehydration reactions (De la Rie et al., 1989; Carbó et al., 2008). Specifically, products with double bonds C=C in conjugation with C=O groups are possibly formed during these reactions resulting therefore in increase of the absorbance at ~270 nm.

The FTIR results support the above spectroscopic observations. Infrared spectra of the initial material (see structure in Table III) exhibited the characteristic bands corresponding to hydrocarbon skeleton (two intense bands ν_{as} of $-CH_2$ at 2926 and ν_s of $-CH_2$ 2855 cm^{-1},) hydroxyl (broad band at 3500–3250 cm^{-1}) and ketone groups (1710 cm^{-1}). A moderate band at 1448 cm^{-1} was assigned to the symmetric bending vibration of $-CH_2$ groups. Finally, a weak band at 947 cm^{-1} was assigned to the cyclohexane ring vibrations, while the medium bands at 1168 and 1067 cm^{-1} can be assigned to the C-O stretching modes in alcohol and the bending vibration of $-C-(C=O)-C-$ groups of the cyclic ketone, respectively (Carbó et al., 2008) (Figure 15). Assignments of infrared spectra recorded from Ketone Resin N film at its initial state are shown in Table IX.

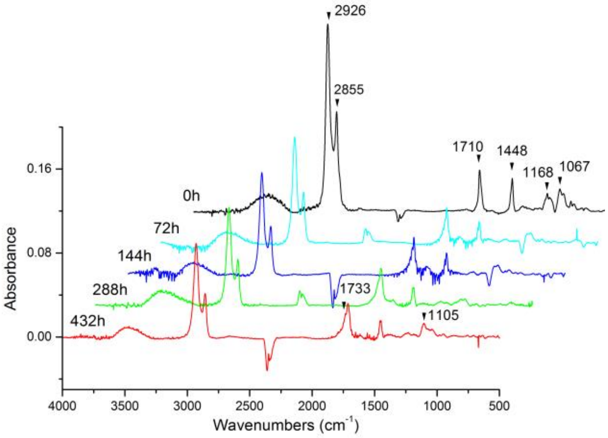


Figure 15. FTIR absorption spectra of Ketone Resin N 10 % (w/w) in THF. During different times (0-432 hours) of thermal ageing at 100 °C

Significant chemical changes associated with thermal ageing were shown through with FTIR (Figure 15). In particular, the broad band of OH stretching (3500-3250 cm^{-1}) decreases upon thermal ageing, whereas a small peak at 1617 cm^{-1} attributed to C=C stretching appears. A significant decrease in the intensity of C–H stretching (2926 and 2855 cm^{-1}) was also observed. These FTIR changes clearly indicate mass loss and dehydration reactions taking place inside the resin films during thermal ageing.

In addition to the above, the C=O stretching band (1710 cm^{-1}) broadens and shifts towards higher wavenumbers (1733 cm^{-1}) whereas a weak - medium band at ~1105 cm^{-1} is formed assigned to stretching of newly produced C-O bonds. These specific changes indicate formation of ester groups.

Laropal A81

SEM morphological examination of Laropal A81 film, in the initial state, revealed that the film had good adhesion to the substrate, while the surface was clear of any type of insoluble material. Thermal ageing induced however, perforation of the film, showing different sizes of rounded shaped holes (<3μm size) (Figure 16), clearly visible even at low magnification. An extensively thickness reduction by 30 % was also observed (Table VIII). This can be attributed to loss of material and partly from solvents evaporation through the formation of volatile products; as can been seen from the following results of spectroscopy.

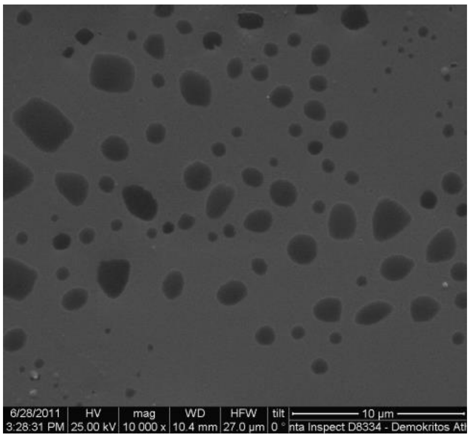


Figure 16. SEM micrographs Laropal A81 film coated by air brush or hair brush on glass slide substrate showing, perforation of resin's film after thermal ageing

The Tg value of Laropal A81 film sample in initial state was recorded at 22 °C, while after thermal ageing this was raised to 45 °C (Table VIII); a Tg value of 57 °C is reported by the manufacturer. The approx. 23 °C temperature change after thermal ageing can most possibly be attributed to solvent evaporation causing changes of resin's free-volume; the possibility of thermal degradation in its first stages cannot however be ruled out.

After thermal ageing Laropal A81 was found to be soluble in the more polar solvents mixture. Swelling and solubility tests after ageing indicated significant reduction of its solubility 7 % (Table VIII).

After thermal ageing an increase (10%) in the water-film surface contact angle was observed, indicating a small increase in film surface hydrophobicity and change of surface polarity (Table VIII). An explanation for this apparently contradicting result is being offered by FTIR spectroscopy (see below).

Colorimetric measurements of Laropal A81 showed colour stability during the 432 hours thermal ageing, with only a minor difference on b* (from 4.28 to 4.87, ΔE= 2.21), indicating slight difference in yellow hue.

The UV absorption spectrum of the material in its initial state showed a peak at 225 nm with no other features in the range 257-800 nm. After thermal ageing at 100 °C for 288 hours, insignificant changes in the UV-Vis absorption spectra were recorded. Upon further ageing, the UV spectra of Laropal A81 exhibited a small increase in film scattering probably, possibly due to enclosure of volatile decomposition products and/or air.

TableVIII. Examination methods for investigating thermal stability of Laropal A81

Thermal ageing – Laropal A81			
Examination method	**Reference material**	**Aged**	**Notes**
Micro-profilometry Films formed by spin coating	817 nm	570nm	Reduce thickness 30 %
Feller Test (solubility test) Films casted on glass slide	Cyclohexane 100 % Teas parameter (fd) N 94	Cyclohexane 75 % Toluene 25 % Teas parameter (fd) N 88	Reduce solubility 7 %
Swelling by weight loss (%) Films casted as membrane	Distilled water 0.16 Isopropanol 0.18 Toluene 2.31	Distilled water 0.16 Isopropanol 1.66 Toluene 2.14	
Contact angle Films casted on glass slide	70	77	Increased 10 %, more hydrophobic
DSC Tg Films casted as membrane	Tg = 22 °C (0.1571J/g/°C)	Tg = 45 °C (0.1747J/g/°C)	Tg 57 °C as report on Technical Datasheet

Infrared spectrum of Laropal A81 in its initial state (see structure in Table VI) included peaks at 2963 and 2874 cm^{-1} due to asymmetric and symmetric stretching vibrations of C-H bonds in the $-CH_3$ and $-CH_2$ backbone groups; ester and tertiary amide carbonyl absorptions at 1734 cm^{-1} and 1653 cm^{-1}; methylene CH_2 vibrations at 1489 and 1457 cm^{-1}, symmetric stretching absorptions of CH_3 at 1390-1369 cm^{-1}, the C-N stretching vibrations in the amide groups at 1311 cm^{-1}, ester C-O bonds at 1264 cm^{-1}, deformation of geminal methyl groups at $C(CH_3)_2$ at 1218 and 1154 cm^{-1} (Zhang et al., 2009). Assignments of Laropal A81 infrared spectra are shown in Table IX, which refer to 0 h in the spectra of Figure 17.

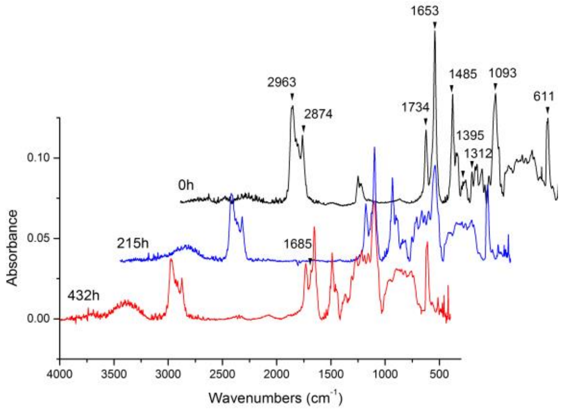


Figure 17. FTIR spectra of the Laropal A81 10 % (w/w) in THF. During different times (0-432 hours) of thermal ageing at 100 °C

FTIR spectrum during and after ageing indicated significant chemical changes, as shown in curves of 215 h and of 432 h on Figure 17. Reduction in absorption intensity throughout the entire spectrum range was observed after 288 hours of ageing.

More specifically, significant decrease of the ester carbonyl absorption at 1734 cm^{-1} was observed, together with formation of tertiary amide carbonyl (1653 cm^{-1}, with a shoulder at 1685 cm^{-1}). Additionally, an increase of the C-N absorption at 1312 cm^{-1} was marked. In addition, considerable reduction of the alkyl group vibrations is observed at 2963 and 2874 cm^{-1} (stretching) and 1485 and 1459 cm^{-1} (bending). The combination of these observations, along with the observation of the perforated film surface (Figure 16) and the scattering in the UV-visible spectrum suggests emission of volatile products, possibly due to scission of the N-(C=O) bond with simultaneous formation of formaldehyde and urea; this suggests partial depolymerisation of the material (De la Rie, 2002; Sathammer et al., 2010). These observations indicate significant overall loss of material and confirm the above mentioned reduction of thickness by 30%. Additionally, a broad absorption at 1300-1150 cm^{-1} is formed, possibly due to the formation of C-O bonds, along with the broad OH stretching band (3300-3200 cm^{-1}) indicative of hydroxyl formation. Finally, formation of carboxylic acids (features at ca. 1705 cm^{-1}), is observed in the aged material, being is another evidence of oxidative degradation processes. This has been previously reported in literature (Lazzari et al., 2000; Chiantore et al., 2001; Cocca et al., 2004) and it is believed that it is related to polarity changes of the resin upon ageing, also confirmed by contact angle measurements (see above).

4. CONCLUDING REMARKS

This work offers a combination of morphological and physico-chemical characterization of the acrylic cyclohexanone-based and urea-aldehyde resins, followed by the investigation of the changes occurred during and after accelerated thermal ageing.

The accelerated thermal ageing of the resins demonstrated the enhanced stability of the acrylic copolymers against structural degradation, compared to those of the cyclohexanone based resins, though all resins display changes of their physical characteristics.

In all cases the ageing time parameter was a crucial factor significantly affecting the performance of resins.

The decomposition process of resins after thermal ageing was responsible for colour changes by yellowing, reduction of film thickness, changes of solubility and swelling.

The main outcome of this study is that acrylic polymers (such as Paraloid B72 and Primal AC33) display higher thermal stability compared to Ketone Resin N, as well as its counterpart, Laropal A81.

Throughout this work, specific differences in the behaviour of the materials have been marked. More specifically, Paraloid B72 was significantly stable through the thermal ageing cycles, with only small chemical structural changes, showing only slight yellowing and reduction of solubility.

Primal AC33 was found to be less stable compared to Paraloid B72, since after 144 hours of ageing, chemical alterations, along with changes in optical properties and reduction of solubility were shown to be occurred. An explanation possibly lies with the lower methacrylate percent of the former material, and presumably explains why the manufacturer has taken this specific product out of the market.

Ketone Resin N was the most vulnerable of the four resins, exhibiting significant degradation and chemical structural changes leading to mass loss, carbon chain unsaturation and ester formation as result of dehydration and subsequent autoxidation reactions. These changes were accompanied by considerable colour change, reduction in solubility and film thickness.

Laropal A81 developed significant morphological (perforation) and optical (scattering) alterations, along with intense thickness reduction as a result to thermal ageing followed by the formation of small volatile compounds. Furthermore, formation of species containing functional groups such as hydroxyl, ketones and carboxylic acids were observed.

Extensive surface cracking of films, even at their initial stages, along with the observed presence of components such as NaCl and TiO_2, need to be considered concerning the methodology of their application prior to the use of these materials on works of art.

The cases where extensive cracking was observed in all four resins films before ageing should be taken under consideration, as it may limit their usage in uncontrollable environmental Stable environment can be considered only the museum environment which is the ideal environment for the exhibition and storage of art works; by providing appropriate and controllable environmental conditions (temperature 20 ±2 °C, humidity 50 ±5 RH, light 200 ±50 lux and 75 μW / lm, air pollution and pest control).

Finally, as a general remark, differences in Tg values measured in the initial states of all resin films as compared to the ones given by the manufacturing companies, were observed. This can be attributed to factors, such as film dimensions and condition of the sample, the used method and the measurements conditions and the used solvents, plasticizers and inorganic fillers. As details of the practice methodology are not given on technical data sheets, the exact explanation for this discrepancy is still open.

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Table IX. Main IR absorption bands (Wavenumbers, cm^{-1}) of resins in initial condition

Paraloid B72	Primal AC33	Ketone resin N	Laropal A81	Comments
Methyl acrylate / ethyl methacrylate	Ethyl acrylate / methyl methacrylate	Cyclohexanone	Urea-aldehyde	Chemical Groups
		3500-3250	3300-3200	O-H groups
2900-3000	2900-3000			C-H stretching
			2963	v_{as} and v_s vibrations of C-H bonds in CH_3 and CH_2 groups at resin skeleton
		2926		v_{as} vibration of $-CH_2$ from hydrocarbon skeleton
			2874	v_{as} and v_s vibrations of C-H bonds in CH_3 and CH_2 groups at resin skeleton
		2855		v_s vibration $-CH_2$
		1710		C=O stretching (ketone)
1733	1734		1734	C=O stretching (ester)
			1653	ester C=O and C-H bonds in aldehyde groups
			1489	methylene CH_2 vibration
			1457	methylene CH_2 vibration
		1448		symmetric bending vibration of $-CH_2$
1448	1448			C-H bending
1388	1387		1390-1369	v_s vibration $-CH_3$
			1311	C-N stretching vibration in the amide groups
1238	1238		1264	C-O ester stretching
			1218	deformation of geminal methyl groups at $C(CH_3)_2$
		1168		v_s C-O in hydroxyl groups
			1154	deformation of geminal methyl groups at $C(CH_3)_2$
	1176			C-O ester stretching
1161	1161			C-O ester stretching
		1067		bending vibration of -C-(C=O)-C- groups of cyclic ketone
		947		cyclohexane ring vibration
			611	ring absorptions

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