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Effect of solvent on PARALOID[®] B72 and B44 acrylic resins used as adhesives in conservation

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Abstract

Paraloid[®] is one of the most frequently used acrylic polymers, employed mainly for its adhesive and consolidating properties in the conservation of a wide range of materials. Appreciated for its reversibility, mechanical characteristics and ease of use, application of the polymer requires it to be simply dissolved in a solvent. Nevertheless, the chemical nature of the relevant solvent must be regarded as an essential parameter, due to its influence on the physico-chemical characteristics of the resulting adhesive film. The aim of this study was to evaluate the effect of the solvents used with Paraloid[®] acrylic resin on adhesive film properties, and more specifically on their thermophysical characteristics. Two compounds used in conservation (Paraloid[®] B72 and B44) and six solvents (ethanol, acetone, ethyl acetate, ethyl lactate, butyl acetate and toluene) were used to make adhesive film replicates. Thermogravimetry and differential scanning calorimetry (DSC) analyses allowed us to determine the value of the glass transition temperature (T_g) of solvent/Paraloid[®] mixtures. Mass monitoring of the films enabled us to correlate T_g values with the quantity of residual solvent. Results showed that all the solvents remained present for a long time in Paraloid[®] films when drying took place at room temperature. Moreover, DSC analysis highlighted the fact that residual solvent had a considerable impact on the value of film T_g. In fact, residual solvent significantly lowered the T_g value of Paraloid[®] (by up to 30 °C below its theoretical value). This underlined the importance of taking the impact of solvent on resin properties into account.

Keywords: Acrylic resins, Paraloid[®] B72 and B44, Solvent, Glass transition temperature

Introduction

Over the last few decades, acrylic resins have been one of the most widely-used materials in conservation. Restorers use these resins, known as Paraloid[®] (or Acryloid[®] in USA), as a coating, consolidant or adhesive because of their relative stability, transparency, mechanical resistance and reversibility [1, 2]. They are suitable for all types of material: metals, stone, wood, glass or ceramics [3]. The most frequently used resin is Paraloid[®] B72. Many recent studies confirm the good qualities of Paraloid[®] for different restoration treatments [4–8]. Paraloid[®] is very used as a reference when testing or studying new products [9–15]. Its preparation depends on its intended function (protection, consolidation or adhesion) and use. Koob [2] has optimized the preparation and application

of Paraloid[®] B72 as an adhesive for ceramics; he highlights the importance of choosing the right solvent for appropriate workability. He recommends the use of acetone (with a 70/30 ratio of acetone/Paraloid[®] B72), but other solvents, such as ethanol, toluene, xylene or ethyl acetate [16] may also be used by restorers. Paraloid[®] B72 is a copolymer of ethyl methacrylate (EMA) and methyl acrylate (MA) with a ratio of 70/30. However, analysis by GC–MS (gas chromatography–mass spectrometry) of the commercial product revealed that an additional compound, butyl methacrylate (BMA) made up 2% of content [17]. According to Horie [3], it is possible to make an acrylic resin with the required physical properties, just by selecting a different monomer. Many acrylic resins are available on the market: for example, Paraloid[®] B44, B48N, B66, B72 and B82 [17]. However, their composition is not always as clearly specified as that of Paraloid[®] B72; thus Paraloid[®] B44, also widely used in conservation, is sold as poly (-methyl methacrylate) (PMMA),

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but analysis carried out by Chiantore et al. [17] revealed it to be a copolymer of methyl methacrylate (MMA) and ethyl acrylate (EA) in unknown proportions. It is easy to adapt the properties of the resin to circumstances and the type of application [16]. Restorers choose a specific resin according to how it is to be applied (adhesion, protection or consolidation) and the materials (porous, such as ceramics, or non-porous such as porcelain). They adjust the concentration of the resin and the choice of solvent: too low a concentration may result in unfilled spaces, and too high a concentration leads to reduced resin penetration [18–20]. The choice of a volatile solvent, such as acetone, also impedes resin penetration; a less volatile solvent, such as toluene, improves the degree of resin penetration into the material, allowing it to be effectively consolidated [16]. The choice of resin, however, should also take into consideration relevant environmental conditions. Ageing studies have integrated environmental conditions, focusing on UV radiation as the main parameter [21]. Nevertheless, environmental conditions, in particular temperature, are a determining factor in the choice of resin because room temperature must be higher than the T_g of the resin [22, 23]. Alexiou et al. [23] performed measurements of mechanical properties at 0 °C, 30 °C and 50 °C, and showed that Paraloid[®] B72 gives poor results at higher temperatures. The use of Paraloid[®] B72 as a ceramic adhesive proved unsuitable in Greece (where summer temperatures are around 40 °C) and in hot climates, as might be expected from its low T_g. Paraloid[®] B72, manufactured by Rohm and Haas, has a T_g of 40 °C, a value very close to summer temperatures in the Mediterranean. This value, provided by the manufacturer, may differ from measurements recorded in experiments: a range value reported between 37 and 41 °C [22], but Paraloid[®] B72 is known to soften at 30–35 °C [1]. These studies are past, but to our knowledge, the most recent work on Paraloid are student reports that have not been published. Glass transition temperature is an important phenomenon in polymer studies [24]. Chapman et al. [16] define T_g as “that temperature at which the available thermal energy is smaller than the forces holding molecules together. At lower temperatures, very little molecular adjustment is possible. Below its T_g, an amorphous polymer is brittle and hard; above its T_g, it is softer and can be dissolved more easily.” This temperature characterizes the change of the resin from a solid, ‘glassy’ state to a softer, ‘rubbery’ state [22]. It is difficult to compare T_g data taken from different literature references; few references state the method used to determine T_g, the measurement parameters, or the conditions of sample preparation (solvent, drying time and drying conditions prior to measurement). These parameters can have a significant impact on the value of T_g. Currently,

restorers choose their adhesive according to the T_g values provided by manufacturers, without taking the impact of residual solvents into account. So, for the reconstruction of a Tang dynasty model of a horse, Ramakers [25] chose Paraloid[®] B44 as an adhesive in order to benefit from a T_g that is higher than Paraloid[®] B72 and well above room temperature. At Arc’Antique, we aimed to test mixtures of Paraloid[®] B44 and B72 but first it was necessary to determine the T_g of these adhesives. Different laws of mixtures have been proposed to describe the evolution of T_g for miscible mixtures. The best known of these are Gordon Taylor’s and Fox’s Law [26]. Gordon Taylor’s Law applies to copolymers, but can be extended to polymer mixtures:

$$T_{g,m} = \frac{\varphi_1 T_{g,1} + K(1 - \varphi_1) T_{g,2}}{\varphi_1 + K(1 - \varphi_1)} \text{ with } K = \frac{\rho_1 \Delta \alpha_2}{\rho_2 \Delta \alpha_1}$$

with T_{g,m} the glass transition temperature of the mixture, T_{g,1} the glass transition temperature of Paraloid[®] B72, T_{g,2} the glass transition temperature of Paraloid[®] B44, φ_1 the mass fraction of Paraloid[®] B72, ρ_1 and ρ_2 the density of Paraloid[®] B72 and B44, α_1 and α_2 the coefficient of the linear thermal expansion of Paraloid[®] B72 and B44.

The density of Paraloid[®] B72 is 9,6 lb/gal (1150.3 kg/m³) with α_1 of $6.3 \times 10^{-5} \text{ K}^{-1}$ [27], the density of Paraloid[®] B44 is 9,8 lb/gal (1174,3 kg/m³) with α_2 of $6 \times 10^{-5} \text{ K}^{-1}$ [28]. In our case, Gordon Taylor’s constant is equal to 0.93. As the densities are close, Gordon Taylor’s law can be simplified by Fox’s law:

$$\frac{1}{T_{g,m}} = \frac{\varphi_1}{T_{g,1}} + \frac{(1 - \varphi_1)}{T_{g,2}}$$

The objectives of this paper are to measure the T_g of Paraloid[®] B44 and B72 pure or mixtures. The comparison of the theoretical and experimental values will allow us to evaluate the impact of the solvent’s choice.

Materials and methods

Materials

Copolymers Paraloid[®] B72 and Paraloid[®] B44 are supplied by the CTS company in the form of transparent pellets. The manufacturer provides T_g values of around 40 °C for Paraloid[®] B72 and 60 °C for Paraloid[®] B44. The acrylic resins were mixed in an organic solvent at a ratio of 35/65 (%wt of resin/%wt of solvent). First, the acrylic resin was weighed in a pill bottle, then the 65% of solvent was added. After weighing, the pill bottle underwent immediate hermetical sealing. The proportions thus measured served as references for the calculation of residual solvent contents. All measurements (thermal analysis and mass monitoring) were taken from films with a thickness of about 1 mm. To form these films, a

sample was made from the solvent/Paraloid[®] mixture and 6.5 g of mixture was deposited in a circular silicon mold (5 cm in diameter). The molds were stored for 1 week in minigrip[®] bags, to prevent the solvent from evaporating too quickly and bubbles from forming in the films. Films were formed using several different solvents: ethanol (only with Paraloid[®] B72), acetone, ethyl acetate, ethyl lactate, butyl acetate and toluene. At least 5 films of each mixture were made.

Mass monitoring

The mass monitoring of the films was carried out weekly on the Denver Instrument S-234 weight scale with a precision of 10^{-3} mg. This measurement enabled the retention rate of the solvent within the resin film to be assessed:

At $t=0$, the retention rate of the solvent was equal to

$$[S_{residual}]_{t=0} = \frac{M_{solvent,t=0}}{M_{film,t=0}} = 65\%$$

At t , the retention rate of the solvent was equal to

$$[S_{residual}]_t = \frac{M_{solvent,t=0}}{M_{film,t=0} - M_{film,t}}$$

$S_{residual,t}$ is the retention rate of the solvent, in %wt, at the time t . $M_{solvent,t=0}$ is the mass of solvent, in g, added to the mixture used to prepare the film. $M_{film,t=0}$ is the mass of the mixture, in g, weighed, to make the film. $M_{film,t}$ is the mass of the film, in g, at the time t .

Thermogravimetric analysis (TGA)

Thermograms were recorded with Netzsch STA 449 F3 Jupiter[®] apparatus. The measurements were made on various samples of Paraloid[®] mixtures. The objective was to determine the minimum temperature level for which residual solvent can be fully removed from the films. The heating rate used in this study was $5\text{ }^{\circ}\text{C min}^{-1}$, from $25\text{ }^{\circ}\text{C}$ up to $130\text{ }^{\circ}\text{C}$, $150\text{ }^{\circ}\text{C}$, $170\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$. $200\text{ }^{\circ}\text{C}$ was chosen as the maximum tested temperature to be sure that any polymer degradation (i.e. implying a mass loss) was possible. Other temperatures for isothermal level were gradually decreased from $200\text{ }^{\circ}\text{C}$ according to the measured mass loss at the end of an experiment. If the mass loss did not change, it meant that the temperature could be decreased. The heating rate was chosen to limit the temperature gradient within the sample and to avoid a too large gap between the furnace temperature (i.e. the imposed one) and the sample temperature. The initial $25\text{ }^{\circ}\text{C}$ isothermal step lasted 20 min to ensure the temperature equilibrium, while the length of the final one varied between 40 min and 12 h according to the temperature level. In all cases, analyses were recorded under nitrogen

atmosphere. Each TGA experiment was done on a different sample.

Differential scanning calorimetry (DSC)

DSC measurements were carried out using TA Instruments DSC Q20 or Q200 apparatus to determine T_g . DSC was calibrated using indium standard (99.99% purity) for several heating rates. For each of them, the onset of the indium melting peak and the associated enthalpy was determined and then introduced in the DSC software for appropriate corrections of temperature and heat flux. The furnace was purged with nitrogen gas at a flow of 50 mL/min and the sample mass ranged from 5 to 10 mg. Samples are taken from Paraloid[®] films (with residual solvent) or directly from pellet for pure Paraloid[®] (without solvent). For all DSC analysis, experiments followed the cycle procedure: the sample was cooled down to $-20\text{ }^{\circ}\text{C}$ (ramp: $5\text{ }^{\circ}/\text{min}$) with an isothermal step at $-20\text{ }^{\circ}\text{C}$ for 2 min. It was then heated up to $80\text{ }^{\circ}\text{C}$ (ramp: $5\text{ }^{\circ}/\text{min}$) with an isothermal step at $80\text{ }^{\circ}\text{C}$ for 2 min, and finally cooled down to $25\text{ }^{\circ}\text{C}$ (ramp: $5\text{ }^{\circ}/\text{min}$). On some curves, an effect based on enthalpy recovery appeared because of structure relaxation (physical ageing) during a storage at $T < T_g$ and was a well known phenomenon [29]. It may lead to errors in the determination of T_g [30]. For samples with this small endothermic peak (those after heating in an oven at $150\text{ }^{\circ}\text{C}$), the procedure cycle was repeated 3 times: the endothermic peak disappeared on the last curve.

Results and discussion

Residual solvents in acrylic resins

Mass monitoring curves presented the same general shape for both Paraloid[®] B72 and Paraloid[®] B44 (Fig. 1a, b): a significant evaporation of solvent occurred during the first 3 days, followed by a slower decrease in the mass of the Paraloid[®]/solvent mixture, which finally tended to reach a stable residual solvent quantity. In the case of the most volatile solvent, only Paraloid[®] B72 is miscible with ethanol, the mass of the film stabilized after around 10 days with a residual solvent percentage of 1 %wt. For Paraloid[®] B72 films (Fig. 1a), two solvent groups were defined: the first group was comprised of the most volatile solvents (ethanol, acetone and ethyl acetate) and the second group was comprised of heavier solvents (toluene, butyl acetate and ethyl lactate). All Paraloid[®] B72 films with volatile solvents (1st group) stabilized in mass with a low level of residual solvent (about $1\text{ %wt} \pm 0.5$) within the first 100 days. With less volatile solvents, the residual solvent content was still 5%wt after 150 days; and after 300 days, about 4%wt of Paraloid[®] B72 films still consisted of solvents. For Paraloid[®] B44 (Fig. 1b), the amounts of residual solvent were higher than those

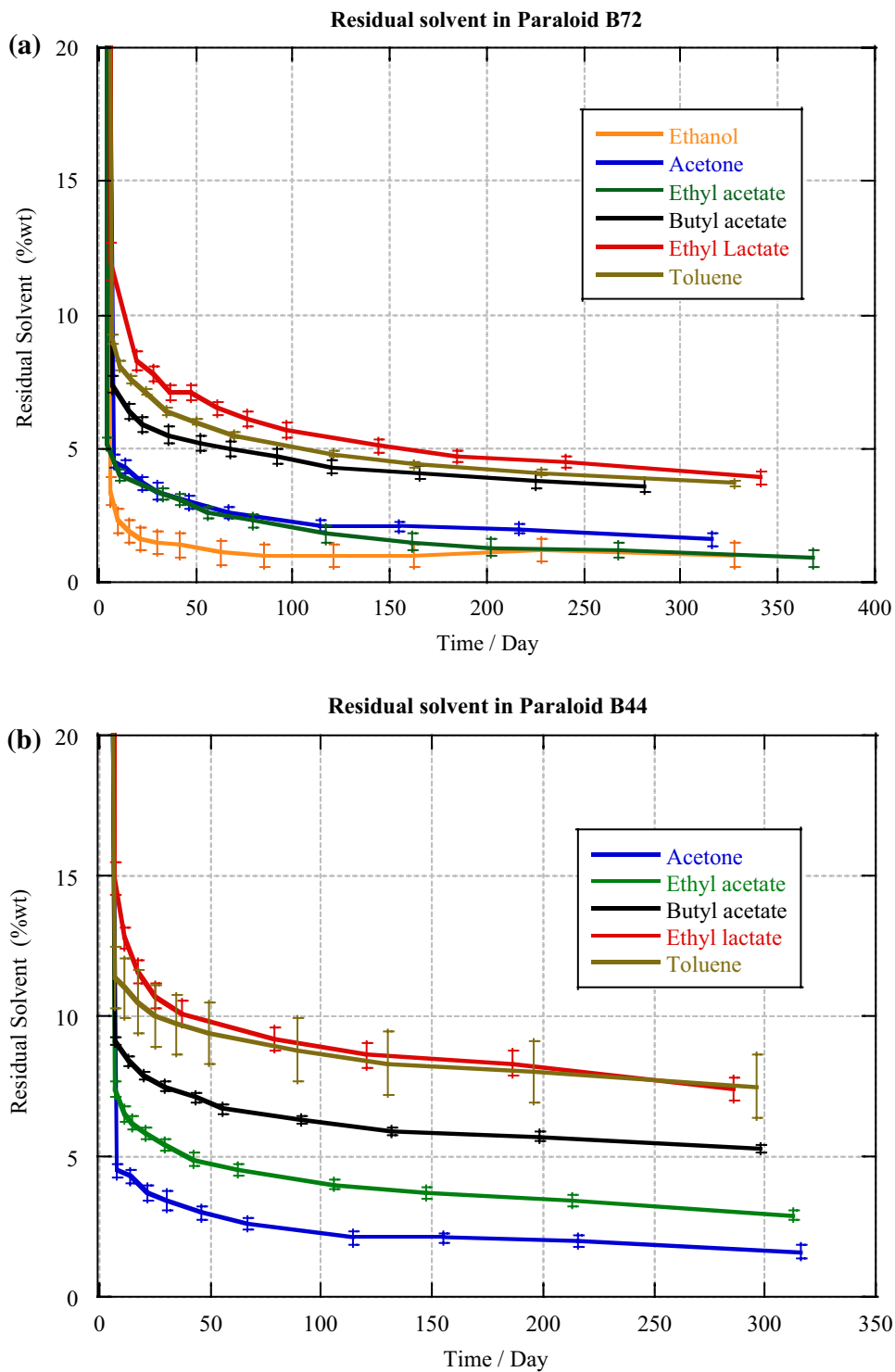


Fig. 1 **a** Monitoring of the mass percentage of residual solvent in a 0.25 mm Paraloid® B72 film as a function of time at 20 °C. **b** Monitoring of the mass percentage of residual solvent in a 0.25 mm Paraloid® B44 film as a function of time at 20 °C

measured for Paraloid® B72: after 300 days, the film formed with acetone contained about 1.5%wt of residual solvent; with ethyl acetate, the residual solvent content was 3%wt, with butyl acetate it was 5%wt, and with toluene or ethyl lactate it was 7.5%wt. The two drying regimes on solvent mass evolution curves (for Paraloid® B72 and B44), irrespective of the solvent used, has been clearly explained by Guerrier et al. [31]:

- In the first part, solvent mass decreases very quickly. During this fast regime, the solvent mass fraction at the air/film interface remains high (>0.25), as does the diffusion coefficient; thus a significant diffusion and evaporation of solvent take place.
- In the second part, solvent concentration, although low at the air/film interface, remains high (<0.25), diffusion becomes too slow to allow sufficient regeneration of the solvent near the interface. The diffusion coefficient changes according to the polymer/solvent ratio. The evaporation flux of solvent becomes very weak and the concentration gradient decreases.

The kinetics of these two regimes depend on the solvent because the evaporation flow corresponds to the solvent’s molar mass, density, vapor pressure, drying temperature and diffusion coefficient [31]. According to the characteristics of the solvents tested (Table 1), the fastest drying rates of Paraloid® films corresponded to the smallest molar masses, the lowest densities and the highest vapor pressures:

Acetone > Ethyl acetate > Butyl acetate > Ethyl lactate.

However, ethanol and toluene do not follow the same pattern: ethanol has lower vapor pressure (Pv), higher density and a smaller molar mass than acetone, yet it evaporates more quickly from the Paraloid® B72 film than acetone. Toluene evaporates very slowly whereas its characteristics (Pv, M, ρ) place it clearly between ethyl acetate and butyl acetate. These anomalies are due to the interactions between the solvent and the acrylic resin

[32]. Polymer–solvent affinity is generally estimated by the Hansen solubility parameters (also known as Hildebrand’s solubility parameters). These parameters can reliably predict solvent-polymer affinity when cohesion is dominated by dispersion forces. However, they are not sufficiently accurate for solvents whose polar or hydrogen bonding interactions play a significant role in cohesion. This previous model can therefore be completed by Burrell’s method which classifies solvents into 3 families [32]:

- Poorly hydrogen bonded, like toluene,
- Moderately hydrogen bonded, like acetone or ethyl acetate,
- Strongly hydrogen bonded, like ethanol.

Poorly hydrogen bonded solvents have maximal absorption capacity, thus toluene has a high affinity with Paraloid® and evaporates slowly. Inversely, strongly hydrogen bonded ethanol has minimal absorption capacity, low affinity, and low solubility in Paraloid® B72 (it is actually insoluble in Paraloid® B44), enabling it to evaporate more quickly.

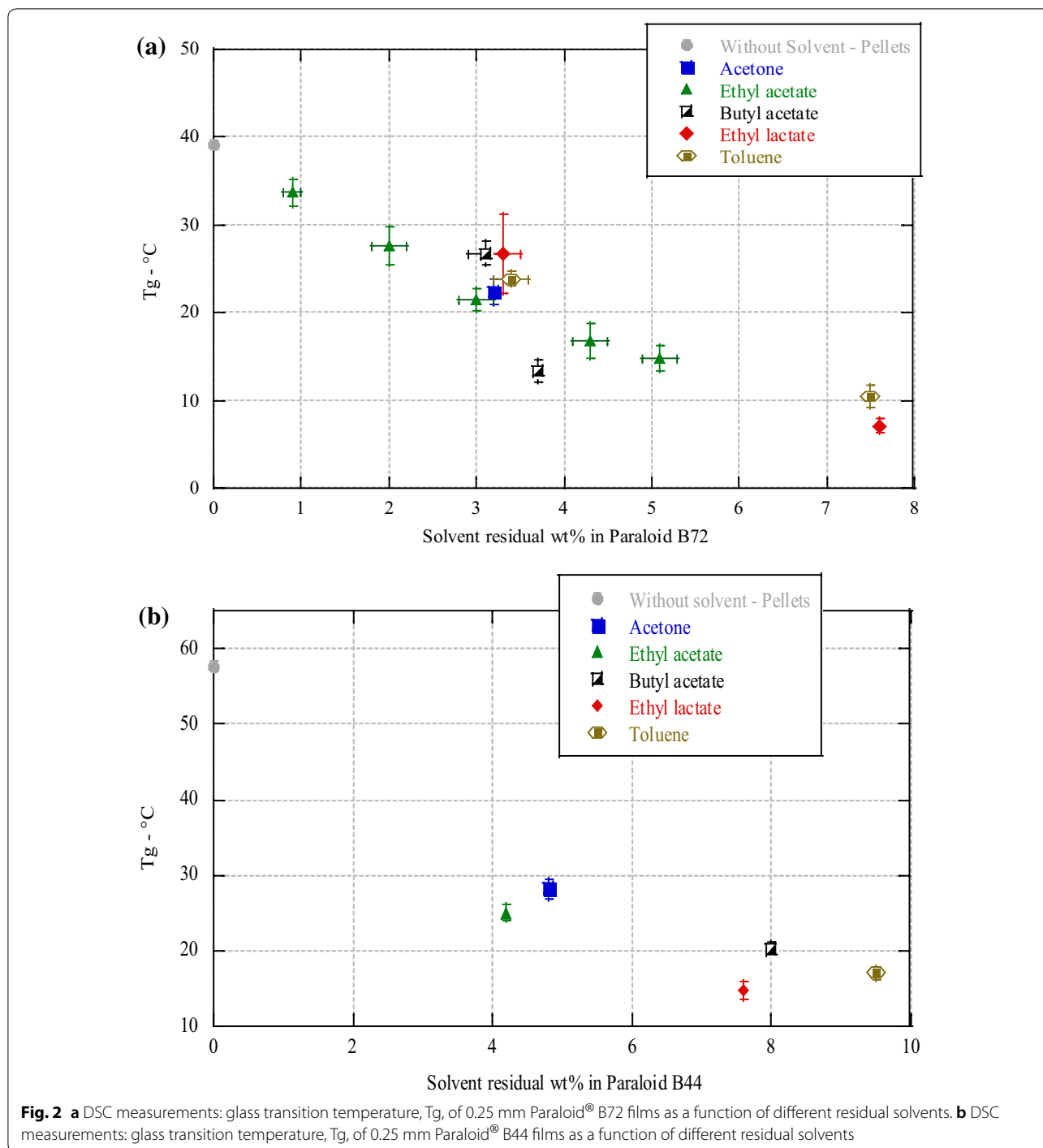
Mass monitoring measurements allow the quantity of residual solvent to be determined: at room temperature, even after more than 300 days, solvent is still present in Paraloid® B72 and B44 films. The quantity depends on the nature of the solvent. To completely remove the solvent, temperature must be increased. Thermogravimetric measurements show that samples must be heated at 150 °C for 40 min to totally eliminate solvent.

Effect of residual solvents on glass transition temperature (Tg)

Tg measurements were taken on pure films of Paraloid® B72 (Fig. 2a) and B44 (Fig. 2b): it was noted that when the quantity of solvent (irrespective of the solvent used) increased, the value of Tg decreased. Glass transition temperatures of both Paraloid® materials were measured directly from pellets provided by the manufacturer: Tg was 39 °C for Paraloid® B72 instead of 40 °C, as specified by CTS supplier data, and Tg was 58 °C for Paraloid® B44 instead of 60 °C as specified by CTS supplier data. In the case of Paraloid® B72, the evolutions of T versus the residual solvent content exhibited the same trend, irrespective of the solvent used. When the amount of residual solvent was about 7.5%wt, Tg dropped to 7–10 °C [case of measurements made with samples prepared with toluene (drying time at room temperature of 20 days) and ethyl lactate (drying time at room temperature of 30 days)]. When the residual solvent rate was about 4–5%wt in Paraloid® B72, Tg was of the order of 15 °C. At 3%wt of the residual solvent in Paraloid® B72, Tg was between 20 and 25 °C. In

Table 1 Characteristics of solvents used: molar mass, M [g/mol] ρ, density (kg/m³), P_v, vapor pressure at 20 °C (hPa)

Solvent	M, molar mass (g/mol)	ρ, density (kg/m³)	P _v , vapor pressure at 20 °C (hPa)
Ethanol	46	798	59
Acetone	58	784	247
Ethyl acetate	88	902	97
Toluene	92	867	30
Butyl acetate	116	882	12
Ethyl lactate	118	1003	2.2



the case of the lowest content of residual solvent and without oven drying (1%wt, case of measurements from samples prepared with ethyl acetate with drying time at room temperature of 1 year), T_g was 34 °C, a lower value than that obtained with samples of Paraloid[®] B72

without solvent. It seems difficult to reach T_g values of pure Paraloid[®] B72 without oven drying. The same effects were seen with Paraloid[®] B44 (Fig. 2b): 8%wt residual solvent decreased the temperature to 15–20 °C instead of 58 °C without solvent. And with 4–5%wt of residual solvent, T_g was between 25 and 30 °C.

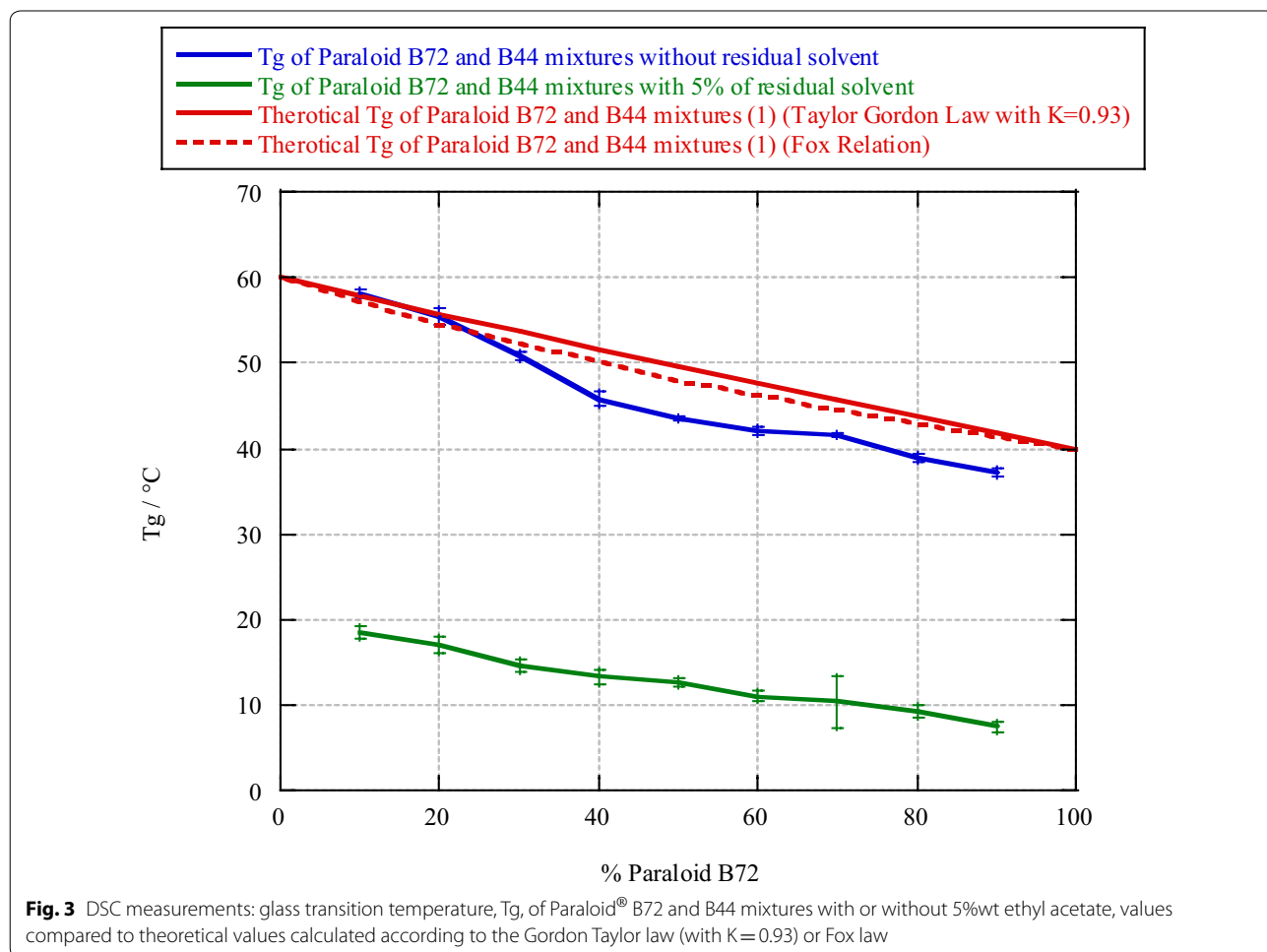
Glass transition temperature (Tg) of Paraloid® B72–B44 mixtures

Glass transition temperatures were measured on mixtures of Paraloid® B72 and B44: the presence of residual solvent had considerable impact on Tg measurements: 5%wt of ethyl acetate in Paraloid® films caused Tg to decrease to around 30° (Fig. 3). However, when films were heated in an oven at 150 °C, solvent was eliminated. The experimental values of Tg are compared to the theoretical values, calculated according to Taylor–Gordon’s law or Fox’s relation (Fig. 2). The curves obtained with these two laws are indeed similar. They give us an initial evaluation of the Tg for Paraloid mixtures, but there is a significant difference between their theoretical and experimental values (ranging between 0 to 5 °C). It is possible to improve these models by taking into account polymer interactions [26]. The equations thus used (polynomials of the 3rd order) narrow the gap between experimental and calculated values. However, the initial approximate evaluation is sufficient for our study. These models confirm the good miscibility of Paraloid® B72 with Paraloid®

B44 and that a mixture of Paraloid® B72 and B44 can be used to obtain a resin with a Tg above 40 °C.

Discussion

Choosing the right solvent to use with acrylic resins in the restoration of ceramics is important because of its long-term effect on the properties of the resin: depending on the nature of the solvent, varying residual amounts will remain present for over a year. Literature has described the plasticizing effect of residual solvent in Paraloid® resins: the use of low volatile solvents favors the presence of residual solvent in acrylic resins [3], and the plasticization effect of residual solvent leads to decreased Tg [1, 21, 33]. Schilling et al. [22] point out that it is difficult to establish a reliable Tg value for Paraloid® B72. The presence of acetone in Paraloid® B72 resins can decrease Tg by several degrees; toluene can lead to a 15 °C reduction, and trichloroethane can cause a decrease in Tg of as much as 25 °C [33]. Our measurements presented in Figs. 1 and 3 correlate Tg values with the quantity of residual solvent and room temperature drying time, the



residual solvent has a significant impact on the Tg values, even several months after the application. According to Bellenger et al. [32], the quantity of solvent in the resin depends on the absorption capacity of the latter. This property varies with hydrogen bonded solvents. The plasticizing role of solvents is essentially dependent on this criterion of solvent absorption. A poorly hydrogen bonded solvent, such as toluene, has thus greater plasticizing efficiency than ethanol, which is a strongly hydrogen bonded solvent. Plasticizers influence the adhesive properties of acrylic resin [34]. They also cause a weakening of intermolecular attractions between polymer chains, with a consequent decrease in tensile strength, a lowering of Tg and an increase in the elongation and flexibility of films. Residual solvents can therefore modify the adhesive properties of Paraloid® by acting as plasticizers, as well as by creating internal stresses (induced by shrinkage) during their evaporation [35]. In our study, we focused on the impact of solvent on Paraloid® films, while the effect of water was not specifically studied. However, a loss of adhesion may lead to an increase of moisture at the film/ceramic interface [34]. The relative humidity parameter should probably be more accurately evaluated and integrated into future studies. To improve the performance of Paraloid® resins, micro-cellulose may be added to increase Tg value [15]. The stabilizing effect of micro-cellulose is probably due to its interaction with the residual solvent.

Conclusions

Acrylic resins, Paraloid®, are among the most widely used resins for restoration, including as adhesives. Several studies have already focused on the choice of solvent in their preparation [2, 16, 36], but these studies focus rather on the ease of use of the solvent/resin mixture than on the impact of the solvent on adhesive film properties. Our measurements of loss of mass show that solvent remains present in Paraloid® film for a long time when drying takes place at room temperature (which is how restorers generally proceed, in particular with respect to ceramics). Paraloid® films with a thickness of about 1 mm must be heated at 150 °C for 40 min to completely eliminate solvent. At room temperature, after 300 days, heavy solvents such as toluene or ethyl lactate, still account for 4%wt of Paraloid® B72 films, and more than 7%wt of Paraloid® B44 films. Light solvents stabilize at lower concentrations, between 1 and 2%wt for acetone or ethyl acetate. The presence of residual solvents modifies the adhesive properties of resin, has a plasticizing effect and decreases the Tg value of Paraloid®. The Tg of Paraloid® B72 can drop to less than 10 °C if the residual solvent rate is greater than 7%wt. With a concentration of 2%wt of residual solvent,

Tg remains below 30 °C, compared to a theoretical value of 40 °C. The impact of solvent on the properties of resins should not therefore be underestimated. Paraloid® B72 and B44 mixtures yield intermediate Tg values, the theoretical value of which can be calculated according to Fox's law, but the influence of residual solvent remains predominant. Further to this study, the mechanical properties of Paraloid® films with established concentrations of residual solvents should be defined to determine which solvent/Paraloid® mixtures are most suitable for use as adhesives on ceramics.

Abbreviations

DSC: differential scanning calorimetry; Tg: the glass transition temperature.

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Authors' contributions

AV and EG designed and performed the research. EB and EG performed DSC analyses. NB monitored a part of analysis. EG wrote the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

All the data supporting the conclusions are included within the article.

Competing interests

The authors declare that they have no competing interests.

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