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Research Article

Science, Engineering and Health Studies
https://li01.tci-thaijo.org/index.php/sehs
ISSN (Online): 2630-0087

Study of alternatives for preserving enamelled goldware using thermoplastic acrylic resin via scientific examination

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***Received**: 22 August 2023*
***Revised**: 3 April 2024*
***Accepted**: 11 April 2024*
***Published**: 14 November 2024*

***Citation**:*
Phukeaw, T., Limpathompipop, T., Chumwong, T., and Girdthep, S. (2024). Study of alternatives for preserving enamelled goldware using thermoplastic acrylic resin via scientific examination. Science, Engineering and Health Studies, 18, 24020004.

ABSTRACT

Four conservation-grade thermoplastic polymers (PB-44, PB-48N, PB-67, and PB-72) were investigated as potential materials for conserving enamel objects. The research aimed to determine the appropriate concentration of Paraloid resin and solvents for forming a film on a silver test plate with a grooved surface. To enhance film visibility, an acrylic green additive, used in King "Ra cha wa dee" enamels, was added. A 20% w/w concentration of Polymer resin with toluene as the solvent showed bubble-free films with no residual resin lumps or pigment additive clumping. The films (PB-44, PB-67, and PB-72) exhibited high transparency, ranging from 98% to 99%, except for PB-48N, which showed a transparency of 77.65%. Each polymer had unique characteristics: PB-44 was strong (Young's modulus of 827.94±50.87 MPa), PB-72 was flexible (elongation at break of 22.10±1.55 %), PB-48N was viscous, and PB-67 had a hard, hydrophobic surface. The films exhibited high thermal stability with degradation temperatures exceeding 200°C and glass transition temperatures over 50°C. They could be readily removed using toluene, acetone, or xylene, without residue. This research provides valuable insights into the properties of Polymer resin films for preserving enamelled goldware, especially in Thailand's tropical climate. These findings are crucial for effective conservation and restoration efforts.

Keywords: thermoplastic acrylic resin; scientific examination; preserving enamelled goldware; substitute material

1. INTRODUCTION

There are many enamelled objects in Thailand, especially using gold vitreous enamel. Some of these date back to the Ayutthaya period. The process of applying gold vitreous enamel is considered a sophisticated and high-level art form in Thai craftsmanship, requiring precision, intricacy, and a high level of expertise from skilled artisans. Vitreous enamel is a decorative technique used to adorn utensils or jewelry made from metals such as bronze, silver, or gold. Instead of embedding real gemstones, colored glass beads, which resemble gemstones but are more affordable, are

https://doi.org/10.69598/sehs.18.24020004

used as decorations on jewelry. It is speculated that Thai craftsmen were influenced by artisans from the Arab and Persian regions who came to trade with Ayutthaya during that the Ayutthaya era. Another hypothesis suggests that Thai artisans may have been influenced by Chinese craftsmen, who, in turn, were influenced by Europeans. Evidence of glass beadwork dating back to the early Ayutthaya period has been found at Wat Mahathat. This was recorded as part of the royal regalia that King Narai the Great bestowed upon King Louis XIV of France.

Decorations with colored glass beads were highly popular during the early Rattanakosin period. This can be seen from the royal regalia created during the reign of King Buddha Yot Fa Chulalok the Great (Rama I). As seen from the goods made for King Rama I, it was popular to use an enamel paint called "Ra cha wa dee." This refers to colored enamel used for the King (Sarapruet, 2019; Thai News Agency, 2019). However, at present, these colored enamel decorations have been found to deteriorate, becoming damaged, and peeling from the object's surface. Figure 1 shows a damaged enamelled gold object, specifically an enamelled gold hairpin called "Phra Jutamanee." It belongs to the early Rattanakosin art period. This rare enamelled gold hairpin is typically worn by Thai royal children during their tonsuring rituals or ceremonies known as "Kone Chook." It is truly upsetting to witness such precious works of art deteriorating over time. Therefore, this hairpin serves as a case study aimed at preserving and continuing the tradition of enamelled goldware; proper conservation methods are crucial to preserving these valuable artworks.

Figure 1. The damaged enamelled gold hairpin, called "Phra Jutamanee"

Enamel techniques found in Thailand can be divided into two categories: Cloisonné and Champlevé. The first enamel technique involves placing gold or copper wires on a metal surface to create patterns. Colored enamels are subsequently dropped into the compartments formed by the wires. The latter enamel technique involves making grooves on metal slabs and then dropping solutions of different colored enamels into those grooves. Both techniques use vitreous enamel (powdered glass, usually mixed with a binder), which fuses a pigment powder to coat the metal surface at temperatures ranging from 500 to 1400°C. The temperatures used for fusing pigment powder in vitreous enamel are mostly between 750 to 850°C, depending on the type of metal and enamel. The most popular colors for enamels are green and red. A wider range of colors has been discovered, compared to ancient times, including shades such as blue, turquoise, milky white, and muted pink. Enamels consist of silicon dioxide (SiO_2) mixed with inorganic metal oxides, which are melted to form colored enameled glass (Spiridonov and Zhukaeva, 2023). For instance, adding copper oxide (CuO) results in shades of green and blue. Mixing cadmium sulfide (CdS) with selenium (Se) produces reddish-orange and orange colors (Praphitphongwanit, 2014). As can be seen, enamel techniques are difficult to produce and require high temperatures, which are clearly not suitable for preserving and conserving enameled objects.

In the study of replacement materials to be used in the restoration of damaged or peeling porcelain, the conservation of enamel gold is essential. This is especially true for the King's enamelled goldware, which has been handed down through generations. This includes items such as the King's insignia, which has unfortunately deteriorated due to the peeling of its enamel coating. Consequently, it is necessary to restore the enamel on the royal insignia to have the most complete pattern for use in royal ceremonies. Therefore, this research aimed to find materials with similar properties to the original enamel, without using heat to melt the enamel on the goldware, in order to avoid damaging the goldware or its surface.

In this work, cold paint made from acrylic epoxy, which is a thermosetting plastic, was avoided. When removed, it can cause significant damage to the original material. Since the colorant must be scraped off, it cannot be removed with a solvent due to the polymeric structure of thermosetting plastics, which are made up of lines of molecules that are heavily cross-linked, creating a rigid molecular structure. Therefore, another interesting group of polymers classed as thermoplastics were considered. Unlike thermosetting polymers, thermoplastic polymers have a non-crosslink structure (Bîrcă et al., 2019), which means they can be dissolved using a solvent without the need to scrape them off.

Thermoplastic polymers are an attractive alternative for preserving enamelled goldware. They belong to another group of polymers that offer promising options for this purpose. They have a linear or branched structure with weak intermolecular forces (Bîrcă et al., 2019). This allows them to be easily soluble, enabling straightforward removal without leaving any scratch marks on an object's surface. They can also soften when heated and solidify upon cooling, making them capable of being melted and reshaped multiple times without undergoing any chemical change, as they lack a permanent crosslinking network.

Nowadays, thermoplastic polymers commonly employed in conservation applications are based on acrylic esters. Their excellent characteristics, including film-forming abilites, mechanical properties, optical clarity, and overall stability, have led to these polymers being extensively utilized in the formulation of paints, surface coatings, and adhesives (Bomin et al., 2018; Lazzari and Chiantore, 2000; Sarapruet, 2019).

Moreover, commercial acrylic resins of conservation grade are produced for the purpose of consolidating and protecting various substrates in monuments and works of art (Amoroso and Furlan, 1975; Down et al., 1996; Lazzari and Chiantore, 2000; Paul, 1996; Thomson et al., 1957). Acrylic polymers and co-polymers are widely used as protective coatings due to their excellent adhesion, hydrophobic properties, chemical inertness, flexibility, brittleness, abrasion resistance, and environmental stability (Amoroso and Furlan, 1975; Carretti and Dei, 2004; Down et al., 1996, Lazzari and Chiantore, 2000; Paul, 1996; Thomson et al., 1957; Tomaszewska and Tomazewska-szewczyk, 2011).

As a result of these properties, they have been extensively employed in the conservation of cultural heritage items since the latter part of the 1960s. In the restoration of artwork, they are applied as consolidants and protectives for various materials, including stones and other porous substances (Vaz et al., 2007; Carrott et al., 1997; Carvalho et al., 2006).

Commercial polymer based acrylic ester resins are known under the Paraloid trade names of PB-44, PB-82, PB-72, PB-48N, PB-66, and PB-67. These are binary copolymers of acrylic monomers, with each type containing a different composition of acrylic units in the polymer structure. For instance, PB-44 contains an ethyl acrylate/methyl methacrylate (EA/MMA) copolymer, while PB-48N is a methyl methacrylate/butyl methacrylate (MMA/BMA) copolymer.

There have been research studies on the properties and decomposition behavior of Paraloids. Chiantore and Lazzari (1996) characterized the chemical structures and compositions of the commercial acrylic resin Paraloids PB-44, PB-48N, PB-66, PB-72, and PB-82, which are used for the protection and consolidation of various substrates. The study revealed that these protective acrylic resins can be distinguished by their refractive indexes and thermogravimetric behaviors. Moreover, they investigated the thermal-aging of various commercial acrylic/ methacrylic resins, including a homo polymer (PB-67) and copolymers (PB-44, PB-82, PB-72, PB-48N, and PB-66), at constant temperatures of 110, 135, and 150°C (Lazzari and Chiantore, 2000). The stability of the resins appeared to be influenced by the reactivity of their alkyl side groups. Overall, the resins exhibited good oxidation stability, with oxygen-containing functional groups observed only in PB-66 and PB-67. The higher reactivity of PB-67 was attributed to the presence of labile tertiary hydrogen atoms on the alkyl side chains, promoting the oxidation process.

Research papers focusing on the application and development of commercial Paraloids, most commonly reported on PB-72 for preservation and conservation applications. Hansen (1995) prepared a PB-72 film and compared it with polyvinyl acetate (PVAC) using solution casting with different solvents. The research findings revealed that toluene promotes pliability, whereas acetone leads to a more brittle material when used as a solvent for PB-72 and PVAC resin. Additionally, the amounts of retained solvent in the polymer films had distinct effects: they caused the glass transition temperature and the strength to decrease, while elongation increased. This increase in elongation was attributed to the retained solvent acting as a plasticizer. PB-72 has also been used in the conservation of materials such as tiles (Vaz et al., 2007), brick (Li et al., 2021), marble, wood, and brass (Ntelia and Karapanagiotis, 2020).

There are few reported instances of commercial polymer-based acrylic ester applications related to enamel-decorated objects. Tomaszewska and Tomazewska-szewczyk (2011) studied the damage of enamel-decorated objects made of copper and copper alloys from the collections of the Regional Museum in Toruń and the National Museum in Poznań. They then consolidated the objects using PB-44 and PF-10 resins (Tomaszewska and Tomazewska-szewczyk, 2011). The study indicated that the resins prevented enamel layer deterioration by filling voids caused by mechanical damage. This resin removal from the surface was also achieved using microfibers soaked in acetone.

Previous research has demonstrated that Paraloid resins can effectively repair initial cracks in colored enamels. However, the addition of coloring additive to these substances, as a substitute for detached enamel, has not been used to enhance their properties. Scientific techniques help conservators choose appropriate conservation methods and materials for preservation and protection of artworks for future generations to appreciate and study (Cocca et al., 2004).

Thus, the aim of this research was to study alternative materials for restoration treatment of enamel objects by comparing the optimal solvent and polymer (resin) concentrations of commercially available conservation-grade thermoplastic polymers (PB-44, PB-48N, PB-67 and PB-72). It does this by determining their physical appearance as films on a silver material surface with simulated deep embossing, along with testing the hardness, strength, morphology, and thermal stability of the Paraloid films. Their efficiency as a substitute for enamel paint as a prepared film, with and without green additives, were discussed considering key polymer properties such as transparency, water-resistance (water contact angle), ease of applicability, viscosity, ease of excess removal, and room temperature applicability. Moreover, this research also evaluated the performance of these materials at different operating temperatures to confirm that melting does not occur at the high room temperatures seen in Thailand.

2. MATERIALS AND METHODS

2.1 Materials

Thermoplastic acrylic resin, specifically the Pararoid resins were provided by the Dow Chemical Company (USA). It is available in four types: PARALOID™ B-44, PARALOID™ B-48N, PARALOID™ B-67 and PARALOID™ B-72. Acrylic green additive was obtained though Rungart CO., LTD, Bangkok). Three solvents, namely acetone, toluene, and xylene, were purchased from Sigma-Aldrich (USA).

2.2 Polymer solution preparation

Four types of Paraloid resins with different concentrations of 10%, 20%, and 30%w/w were dissolved in acetone, toluene, and xylene solvents at room temperature for 4 h using a magnetic stirrer. Subsequently, polymer solutions were obtained, such as PB-44/10%/toluene, which refers to PB-44 with a concentration of 10 %w/w using toluene as the solvent.

Because neat Paraloid films tend to be highly transparent, 10%w/w of a green acrylic additive was added to the polymer solution to make it easier to consider the physical characteristics of the resulting films. The green polymer solution was obtained after using a magnetic stirrer for 1 h. For instance, PB-44/20%/toluene/G refers to PB-44 prepared with a concentration of 20%w/w using toluene as the solvent and 10%w/w of a green acrylic additive.

2.3 The study of suitable concentrations of Pararoid resins and solvent types

The Pararoid resins were mixed at different concentrations (10, 20 and 30%w/w) with different solvents (acetone, toluene and xylene). One g of each polymer solution was dropped onto a test plate made of silver, with a simulated deeply grooved surface measuring 2 cm in diameter and 1 mm in thickness (Figure 2). The plates were dried at room temperature (30.0±1.0°C) for 24 h in a vacuum oven. The suitability of the Pararoid resins and solvent type concentrations were determined based on the screening of the physical appearance in terms of film transparency, foam formation, and dispersion of the green additive. After drying, the films were removed from the plates and stored at (25.0±1.0°C) until characterization.

Figure 2. The silver disc test plate with a deeply embossed surface

2.4 Films characterizations

Polymer films were obtained from a polymer solution derived from various Pararoid resins at 20%w/w (the optimum concentration), both with and without a 10%w/w green additive, using toluene as a solvent (the best solvent). These films were analyzed using the following scientific techniques to compare various properties for evaluation as a substitute material.

Film thickness was measured using a hand-held micrometer (Mitutoyo, Japan) with a sensitivity of 0.001 mm. Ten thickness measurements were taken at various points on each testing sample. Films with a thickness of 200–300 μm were mostly used throughout this study.

The transmittance (%T) and colorimetric parameters of the film samples were measured using Cary Win UV software (Agilent Technologies, Santa Clara, CA, USA). Visual examination of transparency allowed the classification of %T at 550nm into four categories: <30% as opaque, 31%–45% as semi-translucent, 46%–75% as translucent, and >75% as optically clear (Girdthep et al., 2014; Ross et al., 2014).

The colorimetric parameters (CIE Lab; L*, a*, b* and Hue angle; C, and H°) for the film samples were determined using illuminant D65 with a 10° standard observer. L* corresponds to brightness, a* refers to the red-green coordinate (+ve = red, -ve = green), and b* is related to the yellow-blue coordinate (+ve = yellow, -ve = blue). Meanwhile, C represents chroma and refers to color intensity, and H° is a chromatic angle related to color appearance parameters.

Pigment dispersions of the green additive were analyzed using an optical microscope (DP28 digital microscope camera, Olympus, USA). Photographs of films containing the green additive with a 4X magnification capability were obtained.

Morphological characterization of the films was carried out using field emission scanning electron microscopy (FESEM) (Mira 3, Tescan, Czech Republic). The samples were stuck on metal stubs and then coated with gold palladium. SEM micrographs were obtained on thin cross-sections of the films.

The thermal stability of films, in terms of initial, maximum, final degradation temperature, and % weight loss, were recorded using thermogravimetric analysis (TGA) with a Perkin Elmer TGA7 thermogravimetric analyzer, PerkinElmer, United States, under a nitrogen atmosphere, with an 8–10 mg sample for each run. The samples were heated at a rate of 20°C/min, from 50 to 600°C. These results serve as essential indicators of the polymer's thermal stability and offer valuable insights into its performance under varying temperature conditions.

The hardness of films was examined using a Shore D hardness device (RH-250A digital Shore hardness tester, LANDTEK, Chaina) measuring between 0 and 90HA, where higher values denote superior hardness characteristics. This model of testing instrument is customized for hard rubber, hard plastics, and semi-rigid plastics, working in accordance with the ASTM D2240 standard for polymers' durometer hardness testing.

Mechanical properties in terms of the tensile strength, elongation at break and Young's modulus of the films were evaluated by a universal testing machine (NRI-TS500-2S, NARIN Instruments, Thailand) following ASTM Method D882. Initial grip separation was set at 50 mm and the cross-head speed used was 5 mm/min. The tests were performed at 25°C, with seven determinations made for each sample.

The viscosity of a 1 g Pararoid resin in a 20-mL solution of toluene was measured according to USP specifications using a Brookfield LV DV II + Pro Viscometer from BROOKFIELD Engineering Laboratories (USA), with a 61 spindle at 200 rpm under controlled conditions at a temperature of 25.0±1.0°C (Alwossabi et al., 2022).

The hydrophilic properties of the film surface were analyzed by measuring the contact angle (CA). Water droplets with a volume of 2 μL were carefully dispensed onto the film's surface using a USB microscope (model TG500PC2, SHODENSHA), Singapore, and images were collected. The contact angle of water was then measured using ImageJ version 1.8.0.

2.5 Statistical analysis

The properties of the film were obtained with at least three replicates. The replicated experimental results were provided with mean and standard deviation values.

3. RESULTS AND DISCUSSION

3.1 The optimal solvent and polymer concentrations

As seen in Figure 3, four types of Pararoid resin were transparent. To investigate the suitability of the solvents and polymer concentrations, the resins were dissolved using different solvents and polymer concentrations (10%, 20%, and 30%w/w.).

Figure 4 illustrates the physical appearance of the cured film after 24 h. It was found that toluene was the best solvent for obtaining a film without any air bubbles. In contrast, acetone exhibited the highest presence of bubbles. The reason for this is that acetone has a lower boiling point at approximately 56°C, compared to toluene and xylene at around 110.6°C and 144.4°C respectively. Acetone evaporates quickly, and does not allow time for trapped air to escape. In the case of the xylene solvent, the pigment dispersion (green additive) was poor, similar to 20%PB-72/xylene/G and 30%PB-72/xylene/G (Figure 4). The optimal concentration was identified as 20%w/w, as this was easier to apply onto the surface. It was also observed that the resulting film had no residual resin lumps, indicating efficient dissolution of each Pararoid resin in all three solvents. These findings suggest that the film could be effectively removed using solutions of acetone, toluene, and xylene.

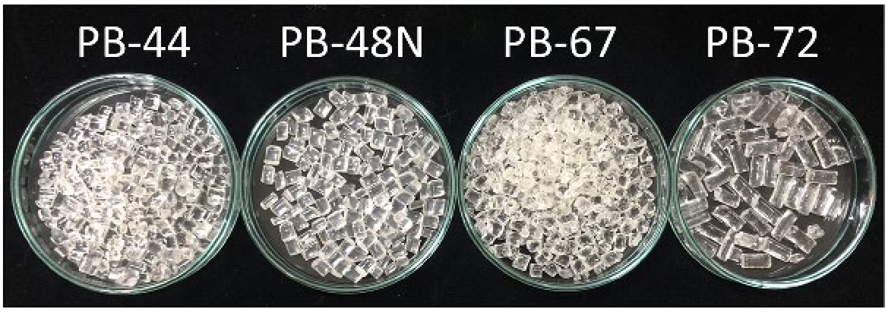


Figure 3. Physical appearance of Pararoid resins

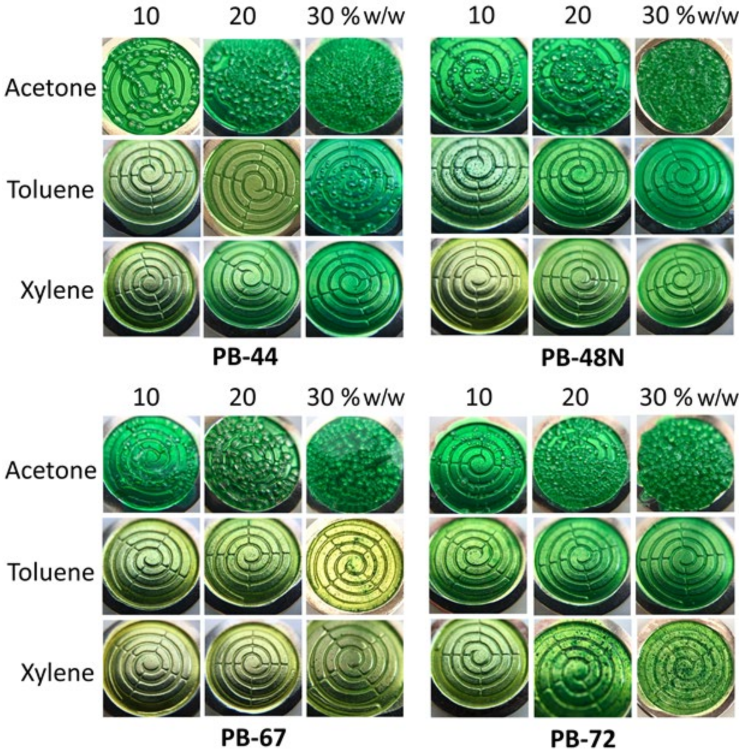


Figure 4. The physical appearance of the Pararoid films after curing on a silver metal test plate

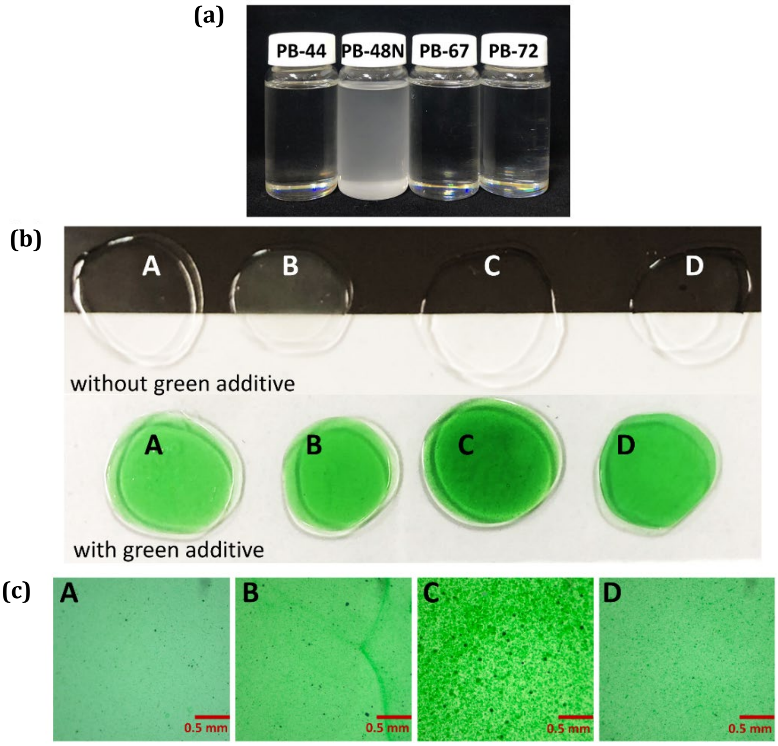


Figure 5. The physical appearance of (a) polymer solution using toluene as solvent and 20%w/w Pararoid resin concentration, (b) the Pararoid films with and without the green additive after drying, and (c) optical images of Pararoid films with the green additive: (A) 20%PB-44/toluene, (B) 20%PB-48N/toluene, (C) 20%PB-67/toluene, and (D) 20%PB-72/toluene

The results showed that toluene was the most suitable solvent, and the most appropriate Pararoid resin concentration was 20%w/w. Subsequently, the Pararoid film was studied by casting the polymer solution (Figure 5a) onto glass plates using toluene as the solvent, with a resin concentration of 20%w/w. This process was undertaken to obtain the Pararoid film for characterization, aiming to evaluate its efficiency of use.

3.2 Physical appearance and color parameter

The physical appearance of the Pararoid films with and without a green additive after drying on the glass are shown in Figure 5(b–c). The thickness of the films ranged from 0.24 mm to 0.37 mm. It was found that the incorporation of the green additive increased the film thickness, as this additive also contained pigment and acrylic polymer constituents (Table 1).

Table 1. Thickness, transmittance and color parameters of the Pararoid films

Films	Thickness (mm)	Transmittance at 550 nm (%)	L*	a*	b*	C	H
20%PB-44/toluene	0.2429±0.0168	99.88±0.15	100.00	0.00	0.52	0.52	89.83
20%PB-44/toluene/G	0.2672±0.0558	77.63±0.18	82.87	-59.44	43.25	73.51	143.96
20%PB-48N/toluene	0.2858±0.0625	77.65±0.60	90.87	0.17	2.03	2.03	85.33
20%PB-48N/toluene/G	0.3795±0.0289	69.93±0.51	77.75	-64.57	50.38	81.90	142.04
20%PB-67/toluene	0.3032±0.0519	98.46±0.21	99.38	0.08	-0.05	0.10	325.82
20%PB-67/toluene/G	0.3628±0.0614	61.93±0.17	72.48	-68.83	56.29	88.91	140.72
20%PB-72/toluene	0.2810±0.0279	98.10±0.18	100.00	0.09	0.02	0.09	12.08
20%PB-72/toluene/G	0.3071±0.0174	70.22±0.14	78.48	-62.41	48.21	78.87	142.31

Pure films of 20%PB-44/toluene, 20%PB-67/toluene and 20%PB-72/toluene without the green additive showed high transparency as optically clear films, with a %T of 99.88±0.15, 98.46±0.21 and 98.10±0.18, respectively (Table 1). On the other hand, 20%PB-48N/toluene exhibited a translucent film with a %T of 77.65, as shown in its translucent solution (Figure 5a). After the addition of the green additive, the dried films showed reduced transparency, compared to the pure films. All film types containing colorants appeared translucent with %T ranging from 61% to 77%. This was due to the presence of pigment particles that cause light scattering (Girdthep et al., 2014). Moreover, it was observed that the %T of 20%PB-67/toluene/G decreased the most, from 98.46±0.21% in 20%PB-67/toluene (without the green additive), to 61.93±0.17%. This phenomenon was due to the poor distribution of the color additive in the polymer matrix, as shown in Figure 5c, resulting in increased light scattering (Girdthep et al., 2014).

As expected, all film types with a green additive appeared green, as is shown in Figure 5b. Compared to films without the green additive, they showed higher a* values ranging from -56 to -68, chromatic angles (H°) between 140–143, and color intensities (chroma, C) between 73–88 (Table 1). This indicated that color shade of the color additive was not affected by any type of Pararoid resin with toluene solvents.

3.3 Morphology

Figure 6 shows SEM images of the cross-sectional regions of different types of Pararoid film. The 20%PB-44/toluene, 20%PB-48N/toluene and 20%PB-67/toluene had relatively smooth fractures. The fracture surfaces of the PB-44, PB-48N, PB-67 films became irregular due to plastic deformation. The 20%PB-72/toluene appeared tougher, corresponding to the mechanical properties results.

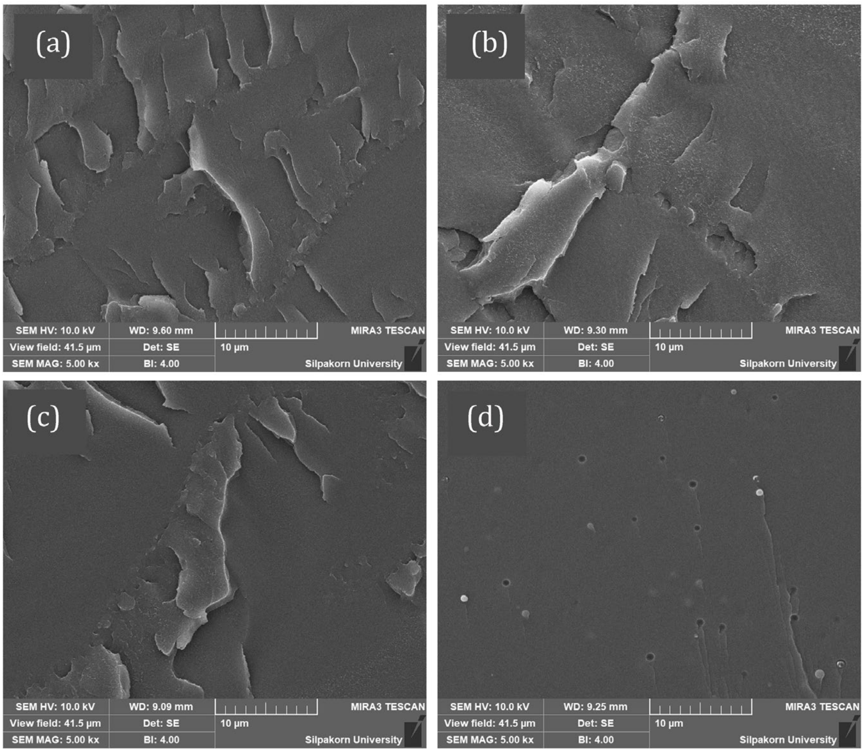


Figure 6. The fractural surface of the different types of Pararoid films: (a) 20%PB-44/toluene, (b) 20%PB-48N/toluene, (c) 20%PB-67/toluene, and (d) 20%PB-72/toluene

3.4 Thermal stability

The thermograms of Pararoid resins are shown in Table 2 and Figure 7, with Figure 7a and Figure 7b representing the weight loss (TGA) and the derivative of mass loss (DTA) curves, respectively. The most important parameters regarding the thermal stability of the investigated materials are summarized in Table 2. The thermal behavior of the Paraloid resins shows distinct differences among the samples, which reflects both polymer compositions and the molecular arrangements of the structural units on the degradation reactions.

Figure 7 and Table 2 also indicate the order of the polymers with the highest thermal stability by considering the $T_{d,\text{ initial}}$ to $T_{d,\text{ max}}$: PB-44 > PB-72 > PB-48N > PB-67. The decomposition process was influenced by the structures and compositions of the copolymers. PB-44, PB-48N, and PB-72 were copolymers, while PB-67 was an isobutyl methacrylate homopolymer (PiBMA). Lazzari and Chiantore (2000) reported that PB-44 may be considered a binary copolymer of ethyl acrylate/methyl methacrylate (EA/MMA) containing a low amount of BMA units, PB-48N is a copolymer of methyl methacrylate/butyl methacrylate (MMA/BMA), and PB-72 is generically indicated by the producer as a copolymer, methyl acrylate/ethyl methacrylate (MA/EMA) (Lazzari and Chiantore, 2000).

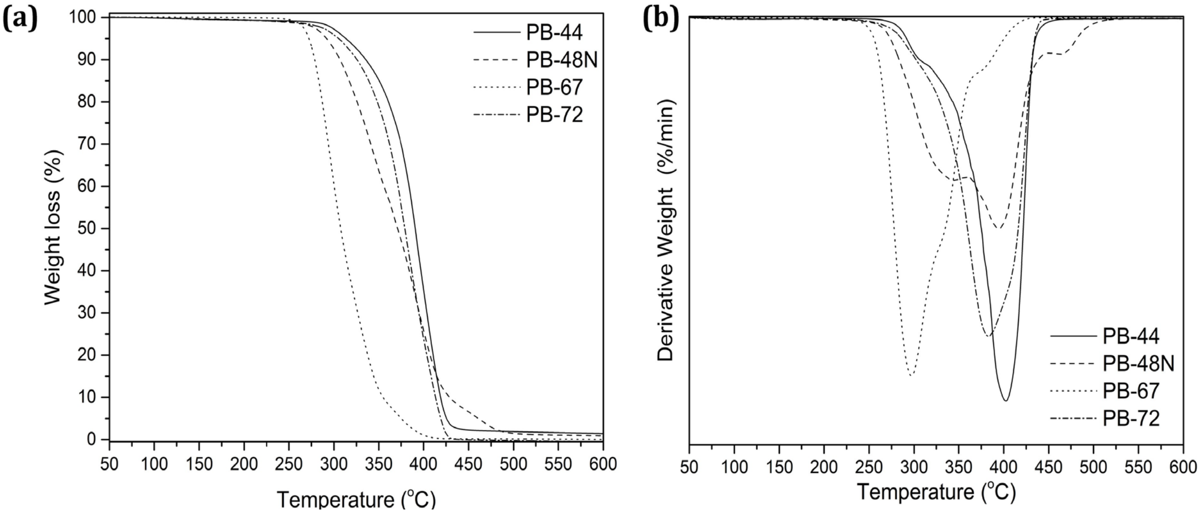


Figure 7. Thermogravimetric analysis curves of (a) weight loss and (b) derivative weight of Pararoid films

Table 2. Thermal stability and mechanical properties of Pararoid films

Films	**Thermal stability**				**Mechanical properties**		
	$T_{d, initial}$ **(°C)**	$T_{d, max}$ **(°C)**	$T_{d, final}$ **(°C)**	**Residual mass (%)**	**Ultimate strength (MPa)**	**Elongation at break (%)**	**Modulus's Young (MPa)**
PB-44	254.89	402.57	453.74	4.669	10.21±0.45	1.29±0.08	827.94±50.87
PB-48N	236.76	398.40	515.38	7.634	15.32±0.78	2.80±0.26	633.89±68.99
PB-67	242.89	296.43	411.43	5.408	n/d*		
PB-72	250.66	382.79	438.02	3.696	11.48±0.96	22.10±1.55	408.32±49.29

Note: n/d = not detected

PB-44 is a random copolymer formed by the structural units MMA > EA > BMA. Its thermal curve shows two stages of weight loss in its decomposition process, which is similar to the thermal degradation of PMMA (with MMA as a monomer). The first step begins at approximately 315°C, which corresponds to the degradation of a small amount of the PB-44 sample. This release involves residual non-reacted monomers encrusted in the polymer (Chiantore and Lazzari, 1996). The second stage ($T_{d,max}$ = 402.57°C) suggests a radical decomposition process, which begins from the end of the polymer chains containing unsaturated bonds in PB-44, regenerating a large amount of monomer from the depolymerization reaction (Godiya, 2019; Thomson et al., 1957).

PB-72 consisted of EMA-MA and MA-BMA random copolymers with the main composition being EMA (EVA > MA > BMA units) (Chiantore and Lazzari, 1996). Thus, the thermal degradation behavior is similar to that of poly(ethyl methacrylate) (PEMA). The first stage at a decomposition temperature of 295.0°C is attributed to the elimination of evaporated molecules in the side groups of polymer chains and the residual non-reacted monomers. The second stage of weight loss at the maximum temperature range of 382.79°C was attributed to quaternized graft chain degradation and decomposition of the backbone polymer (Fares, 2012).

PB-48N exhibited faster thermal decomposition than PB-44 with a $T_{d, initial}$ and $T_{d, max}$ of 236.76°C and 398.40°C, respectively, yet it contained the same unit composition of MMA and BMA (no EA) in the polymer structure. According to Chiantore and Lazzari (1996), this could be attributed to the higher number of BMA units in PB-48N. Thus, the majority of chain scissions occur in BMA sequences, initiating depolymerization that can also progress into the MMA units at temperatures lower than those causing the scission of MMA-MMA bonds.

PB-67, a PiBMA, exhibited a single stage of TG and a single peak on the DTG curve with the $T_{d,initial}$ of 250.66°C and $T_{d, max}$ of 295.32°C. This indicates that the degradation was due to isobutyl group degradation and a random chain scission, with the mass loss of PiBMA beginning at 250.66°C (Habi and Djadoun, 1999; Lazzari and Chiantore, 2000).

3.5 Hardness and mechanical properties

The Shore D hardness of the Pararoids is shown in Figure 8a. Four types of Pararoid were identified as soft plastics, showing a hardness scale between 23 and 25. It was found that PB-44 exhibited a greater hardness than the other Pararoid films.

PB-44 showed the highest clear film hardness, followed by PB-48N, PB-67, and PB-72, corresponding to previous reports (Jessica et al, 2024; Mohamed et al, 2022).

Similarly, the tensile strength results are presented in Table 2 and Figure 8b. It is indicated that the Pararoid film with the highest strength was PB-44, followed by PB-48N and PB-72, respectively. PB-44 exhibited an ultimate strength of 10.21±0.45 MPa, a Young's modulus of 827.94±50.87 MPa, and an elongation at break of 1.29±0.08%. On the other hand, PB-72 showed the greatest flexibility with an elongation at break of 22.10±1.55%. PB48N exhibited a slightly reduced hardness, compared to PB-44, being a Young's modulus of 633.89±68.99 MPa. However, PB-67 could not be cast as a film due to its brittleness.

3.6 Efficiency as a substitute for enamel paint

The selection of the resin, intended to serve as an additive to enhance the pattern and reinforce the enamelled goldware object should be transparent, colorless, elastic, water-resistant, and viscous. It should also be easy to apply, and to remove any excess, at room temperatures.

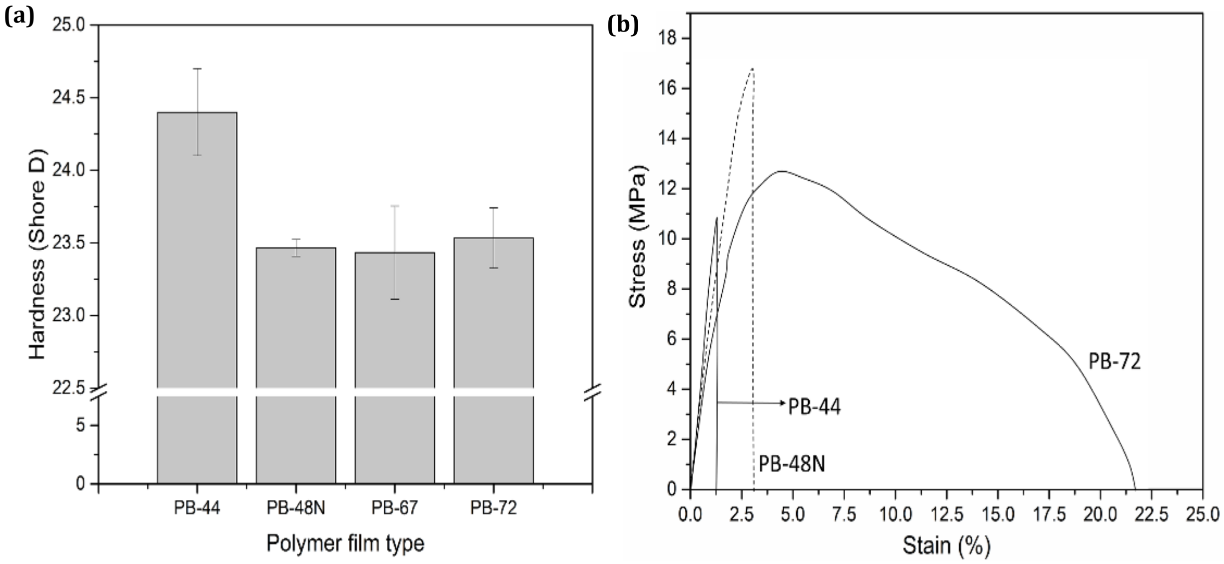


Figure 8. (a) Shore D hardness and (b) stress-strain curve of Pararoid films

The optimal solvent and polymer concentrations investigations indicated that toluene was the most suitable solvent, with a resin concentration of 20%w/w. The resulting film on the surface of the silver plate with deep embossment was also found to be free of residual resin lumps and bubbles.

The preparation of the solution and formation of films through the evaporation of toluene made it easy to apply. Additionally, the solution of PB-48N showed the highest viscosity (Figure 9a), with PB-44 and PB-72 not far behind, while the PB-67 solution exhibited the lowest viscosity in the test. These viscosity findings align with the research reported by Tomaszewska and Tomazewska-szewczyk (2011).

All four Pararoid films showed good clarity (transparency results) and flexibility (hardness and mechanical properties results), especially PB-72 standing out for its exceptional ability to bend and conform to the shape of the enamel layer. Moreover, the resulting film did not change color when color additives were added.

In addition, the water contact angle (Figure 9b) of the four films demonstrated high contact angles with low surface energy, ranging from 73 to 97°, which is consistent with Ntelia and Karapanagiotis's (2020) results. Particularly, PB-67 exhibited a contact angle of 97°, indicating its highly hydrophobic surface characteristics. Therefore, all four Pararoid films exhibited water resistance.

Pararoid films were easily removed using toluene, acetone, and xylene, as they could readily dissolve, leaving no residual resin lumps. Moreover, they could be peeled off from the surface. The physical appearance of the films after peeling is shown in Figure 10. Although the 20% PB-67/T/G film could not be peeled off one piece, it could be easily removed without leaving a trace (Figure 10c). The Pararoid solutions were applied at room temperature, highlighting that they can form as a film through the evaporation of solvent at room temperature (≈ 30°C in Thailand). With comparison to the vitreous enamel technique, this technique did not require high temperatures.

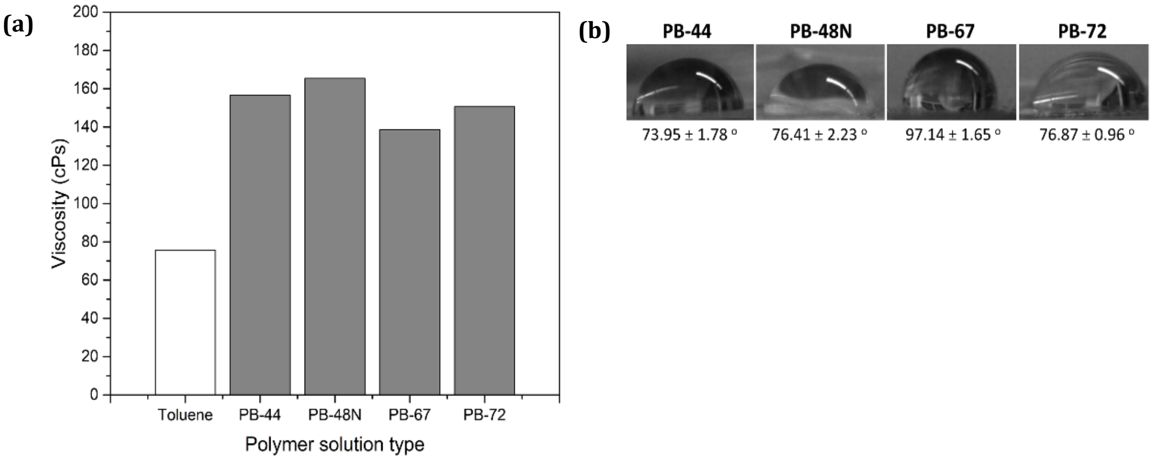
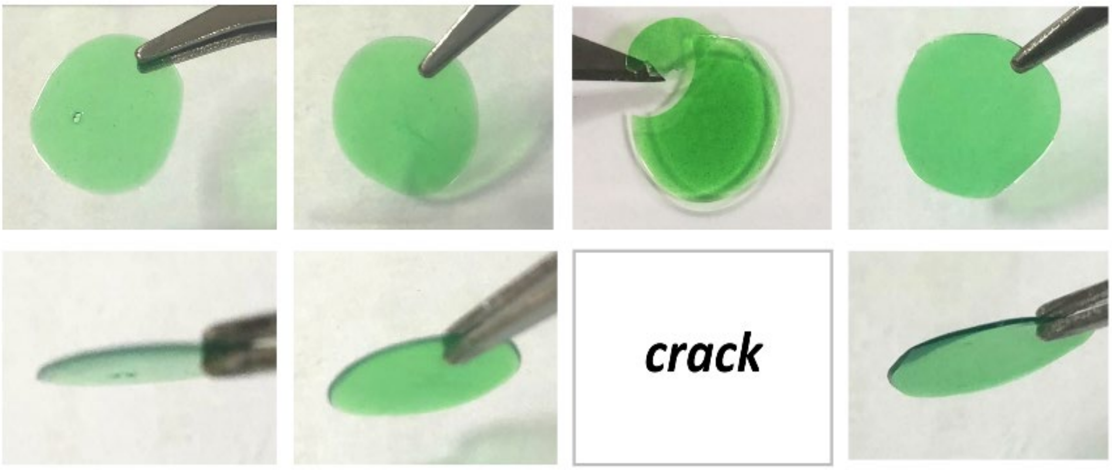


Figure 9. (a) Viscosity of polymer solution of each Pararoid resin and (b) water contact angle of Pararoid films



(a) **(b)** **(c)** **(d)**

Figure 10. Physical appearance of the film after peeling from glass surface: (a) 20%PB-44/T/G, (b) 20%PB-48N/T/G, (c) 20%PB-67/T/G, and (d) 20%PB-72/T/G

The obtained films suggested that PB-48N had a lower thermal stability with the lowest initial degradation temperature of 236.76°C. In addition, the thermal properties in terms of glass transition temperature (T_g) of the Pararoid resins in this research were all greater than 50°C (Vinçotte et al., 2019). This confirmed that the resulting polymer films remained glass-like, with no oozing or melting occurring on the applied surface when applied at room temperature in Thailand (≈ 30°C).

Based on the results, the four Pararoid resins (thermoplastic acrylic resin) with a concentration of 20%w/w, using toluene as the solvent, demonstrated their potential as additives to enhance the patterns of and reinforce the enamelled goldware objects. Consequently, they present as viable alternatives for preserving enamelled goldware.

4. CONCLUSION

The successful study of alternatives for preserving and fulfilling the pattern of enamelled goldware was achieved through scientific examination. Key properties, including viscosity, hardness, heat resistance, transparency, water resistance, and ease of use of Pararoid resin, were taken into consideration to assess their efficiency as a substitute for enamel paint.

Four types of Paraloid resins with green additives were studied to determine the appropriate concentrations and solvents for forming a film on a test plate made of silver with a simulated deeply grooved surface. It was found that toluene is a suitable solvent, and the optimal concentration of Pararoid resin is 20%w/w. The presence of the acrylic green additive improved visibility, enabling observation of bubbles, residual resin lumps, and pigment additive dispersion, as the neat Pararoid film tends to be highly transparent. All Pararoid films were clear and flexible, especially PB-72, which displayed flexibility and bendability. Each type of Pararoid exhibited different characteristics: PB-44 was stronger than the other Pararoid films, PB-48N showed the highest viscosity, and PB-67 film had a hard glassy surface with hydrophobic properties.

Additionally, Pararoid solutions demonstrated applicability at room temperature and could form films through solvent evaporation in Thailand's ambient conditions. Furthermore, these resins displayed thermal stability at temperatures up to 200°C, with a glass transition temperature exceeding 50°C. This confirms that the resulting polymer film remains glass-like, preventing oozing or melting on the applied surface even at room temperature in Thailand, which remains below 50°C.

ACKNOWLEDGMENT

This research is financially supported by Office of the Ministry of Higher Education, Science, Research and Innovation, National Research Council of Thailand, Thailand Academy of Social Sciences, Humanities and Arts (TASSHA) and Thailand Science Research and Innovation (TSRI) National Science, Research and Innovation Fund (NSRF) (Fiscal Year 2022) for Sutinee Girdthep and Titichaya Limpathompipop, and the Faculty of Science, Silpakorn University, Grant No. SRIF-JRG-2566-02 (Sutinee Girdthep).

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