Research paper

Effects of Resins and Adhesives on the Preservation of Converted Handmade Papers

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【Summary】

This study focused on the effects of resins and adhesives on the preservation of a series of dyed handmade papers, called "multi-colored, gold-embossed papers". The substrates included filter paper, lab-prepared handmade papers, and commercial water-patterned handmade papers. The resins or adhesives were impregnated into the papers and then 105℃ dry heat was applied for accelerated aging treatment. Changes in the paper strengths and colors were determined afterward. The results indicated that the paper substrates exerted significant influences. Although the commercial paper upon impregnating with various gelatins could markedly increase its folding endurance, after 12 d of 105℃ dry-heat, however, the folding endurance was almost reduced to 0; tearing strength retention was merely 20%. Thus it was not durable and would not be suitable for use as a medium for artistic creations. Individual resins and adhesives exhibited differing effects; they affected the original strengths of the substrate papers, but also the aging responses and changes in coloration. For tearing strength retention, the 2 wet-strength resins, sodium alginate, alum-added gelatin, and starch showed poorer strengths after the 105℃ dry-heat treatment. Resins or adhesives added with an insolubilizer, AZC, were superior to alum, and the effects were more distinctive in filter paper than in handmade papers, mainly because there was no calcium carbonate in the filter paper to neutralize the acidity of the alum.

Key words: handmade paper, accelerated aging, preservability, applying adhesives.

Shyu JG, Wang KT, Chang CP. 2011. Effects of resins and adhesives on the preservation of converted handmade papers. Taiwan J For Sci 26(3):221-43.

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Received June 2010, Accepted May 2011. 2010年6月送審 2011年5月通過。

研究報告

樹脂及膠對紙張保存性之影響

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摘 要

本試驗研究用於加工特殊染色紙—五色金花紙之樹脂及膠對紙張保存性之影響。藉含浸方式將樹脂或膠施於濾紙、自製手工紙及市售水紋紙等三種紙張，採用乾熱方式進行紙張之加速劣化處理，並測定紙張強度及顏色變化，以評估手工紙之保存性。結果顯示含浸各種動物膠之市售水紋紙雖可大幅增加原始耐摺力，但經12天105℃乾熱劣化，耐折力即降至幾近於0，撕力的留存約剩20% 左右，顯示出難以長期保存，不宜用作書畫藝術用紙。個別樹脂及膠之效果各有不同，不僅影響紙張原始強度，對乾熱劣化之反應亦不相同，紙張之顏色變化亦復如是。以撕力保留率而言，經105℃乾熱劣化後兩種濕強樹脂、鹿角菜膠及添加明礬之動物膠及澱粉，保留率相對較低。樹脂或膠添加耐水化劑，以AZC較明礬為優，這種現象在濾紙較自製手工紙為明顯，主要因為濾紙中沒有含有足以緩衝明礬酸性的碳酸鈣之故。

關鍵詞：手工紙、加速劣化、保存性、施膠。

徐健國、王國財、章之平。2011。樹脂及膠對紙張保存性之影響。台灣林業科學26(3):221-43。

INTRODUCTION

Chinese handmade calligraphic and painting papers have a multi-faceted are very diverse. However, because of the gradual attrition in the preparatory technologies over the ages, and escalating labor costs of artisans producing these papers, many of them are either not available or are becoming increasingly rare. This has led to the common monotonous impression of such papers as being merely variations of black inks on white papers. Calligraphers are eager to try their art on specialty handmade papers, often the folklore of yore. In the developmental history of handmade papers, besides expanding raw materials, and improving papermaking processes, there were also various conversion technique developments which were based on practicality or embellishment needs. For instance, by brushing unboiled soy milk onto a handmade paper, so-called tofu-shuan paper was invented; by pressing several shuan sheets together, the so-called cooked-and-hammered shuan was produced; and by speckling tiny gold foil on handmade paper, the so-called cold-gold sheets were prepared (Tsen 2002). Other modes of conversion include application of a resin/adhesive (Pan 1998), flowing-sand marbling (Wang 2001), waxing, dipping in oil, silk-screen printing, sprinkling with gold and silver slivers, or mica powder, etc. (Chen 1979, Lin 1985). Among these, applying an adhesive to handmade paper is a common conversion technique. Modes of application include impregnation and brushing-on. Although applying adhesives to handmade paper is rather prevalent, there is a lack of systematic study of its efficacy. Therefore, in this study, we examined many traditional agents such as animal glue, starch, acrylic resin, and insolubilizer, and studied their effects on the preservability of handmade papers impregnated with these chemicals. In addition, the effect of retained calcium carbonate in the handmade papers on the acid-buffering capacity of the paper during an accelerated aging process was also examined.

Starch and its derivatives are widely used in the paper industry, as well as the mounting operation of paper-based artworks. Sometimes, for the purposes of smoother operation and functionality, such as insolubility or a longer shelf-life, alum (aluminum sulfate) is often added to starch pastes. However, as alum is acidic upon hydrolysis, its presence is harmful to the preservation of paper. In order to solve this problem, an alkaline insolubilizer, ammonium zirconium carbonate (AZC) is often used to replace alum. There are, however, very few reports that mention the effects of the 2 chemicals on the preservation of paper (Wu 2007). Furthermore, application of wet-strength agents and acrylic resins to substitute the more traditional glues/adhesives might also exert their effects on the preservability of paper, which has also scantly been dealt with in the literature (Wang and Ku 1994).

The paper substrates studied in this project included filter paper, lab-prepared handmade paper, and a commercial water-grained Chinese artwork paper. We opted for filter paper because of its simple composition; the lab-prepared handmade paper has a superior ink-tone; while the commercial paper is the most widely used dyed paper on the market.

In this study, we began by preparing a specially dyed handmade paper, the multi-colored gold-speckled paper, which by applying a simple yet unique staining method, produced multiple grain patterns and elegant appearing converted paper, so as to enrich choices of artists. This special conversion process mainly entailed using various-colored pigments, pearlite pigments, and adhesives to convert a handmade paper furnish. Furthermore, with regard to the individual adhesives, including various natural and synthetic water-soluble resins and glues, were impregnated into the handsheets. Subsequently, the papers were subjected to 105℃ dry-heat accelerated aging treatment to evaluate the effects of the additives on the preservability of the base papers. The results should provide guidance for choosing adhesives. The importance of calcium carbonate to the preservation of paper was also noted.

MATERIALS AND METHODS

In the choice of insolubilizers, food-grade gelatin and starch were respectively added with alum and AZC to examine their effects on paper preservability. Other chemicals additives examined for their preservation efficacies included 2 types of self-cross-linking acrylic resins, P103L and AT40-2; 2 epoxy wet-strength agents, Parez and AF125; a carrageenan glue, λ-carrageenan glue, and sodium alginate. The wet-strength agents were selected based on the frequent need of papers to retain strength and integrity when wet; the influence they exerted on paper durability was thus studied. Incorporation of carrageenan and alginate types of glues was a hold-over from our prior study in the preparation of flowing-sand (marbling) papers, and we also examined their effects on paper durability.

The folding endurance and internal tear strength can serve as indicators of paper preservability after accelerated aging (Ku and Wang 1989). Barrow (1960) noted that heating at 105℃ for 72 h is equivalent to natural paper aging for 25 yr. Kelly (1981) pointed out that after accelerated aging paper at 100℃ for 24 d, the papers that retained 50% of the original folding endurance and 85% of the original tear strength should be deemed to possess good preservability with an expected lifespan of 500 or even 1000 yr. As a consequence, we adopted 105℃ dry-heat treatment as the accelerated aging test.

Materials

Three tested base papers included a commercial filter paper (Advantec no. 131, Tokyo, Japan). The second was a self-made handmade paper using kozo or paper mulberry (*Broussonetia papyrifera*) bast fiber, abaca (*Musa texalis*), longshuitsao (*Eulaliopsis binata*) pulp, and cotton linter pulp in a ratio of 35: 25: 25: 15. The pulp suspension was then sequentially added with 10% calcium carbonate, gelatin, and a wet-strength agent. The third paper tested was a commercial "waterflow" grained handmade paper (Huifongtang Brush and Ink, Taipei, Taiwan).

The resins/adhesives tested included food-grade gelatin (Gelita AG, Eberbach, Germany); chemical-grade gelatin (Hayashi Pure Chemicals, Osaka, Japan); industrial-grade gelatin (First Chemicals, Taipei, Taiwan); and painting-grade gelatin "Sasenbon glue" (Yuren Art Supplies, Taipei, Taiwan). The wet-strength resins of the epoxy type included Parez (Kemira Chemicals, Helsinki, Finland) and AF125 (Taiwan Arakawa Chemicals, Keelung, Taiwan); 2 kinds of self-cross-linking acrylic resins, P103L and AT40-3 (Chanshieh Enterprise, Taipei, Taiwan); food-grade wheat starch (Archer Daniels Midland, Candiac, Que, Canada); and carrageenan, λ-carrageenan, and sodium alginate (Chengchen Food, Taipei, Taiwan). Auxiliary chemicals included alum (Hayashi Pure Chemicals, Osaka, Japan) and AZC (Akzo Nobel, Taichung, Taiwan).

Methods

The 1% resin or adhesive solutions were applied to the above 3 papers using an impregnation (soaking) method. For gelatin and wheat starch preparations, a 0.05% solution of alum or the AZC insolubilizer was also applied. Upon air-drying, the treated sheets were heated in an 105±2℃ oven for 15 min in order for the resins or adhesives to cure properly. One specimen from each treatment was retained as a blank, the rest were subjected to dry-heat accelerated aging at 105℃, and test specimens were removed from the oven at 3, 6, 12, 24, and 48 d. Specimens were tested for paper strength, pH, and change in coloration. The strength parameters were folding endurance (TAPPI standard T511 om-96) and internal tearing resistance (TAPPI standard T414 om-88) tests which are particularly sensitive to paper degradation. The filter paper, however, was too thick, so we were unable to administer the folding test; the tensile strength was tested instead. In all folding endurance tests, the tensile loading on the test strips was 0.5 kg. Brightness and CIE L*a*b* values of the samples before and after the dry-heat aging treatments were determined according to the TAPPI standard T 453 om-89 method.

Instruments

An MIT type folding-endurance meter (Nerima, Tokyo, Japan), a tensile strength tester (Adamel Lhomargy DY 20B, En Brie, France), a spectrophotometer (Minolta CM-3630, Osaka, Japan), a tearing strength tester (Adamel Lhomargy ED 20), a weatherometer aging chamber (Memmert UL 60, Schwabach, Germany), and a pH meter (6173 Janco Electronics, New York, NY, USA) were used in the study.

RESULTS AND DISCUSSION

Tear strength

Figures 1~3 show the effects of base papers impregnated with various adhesives and

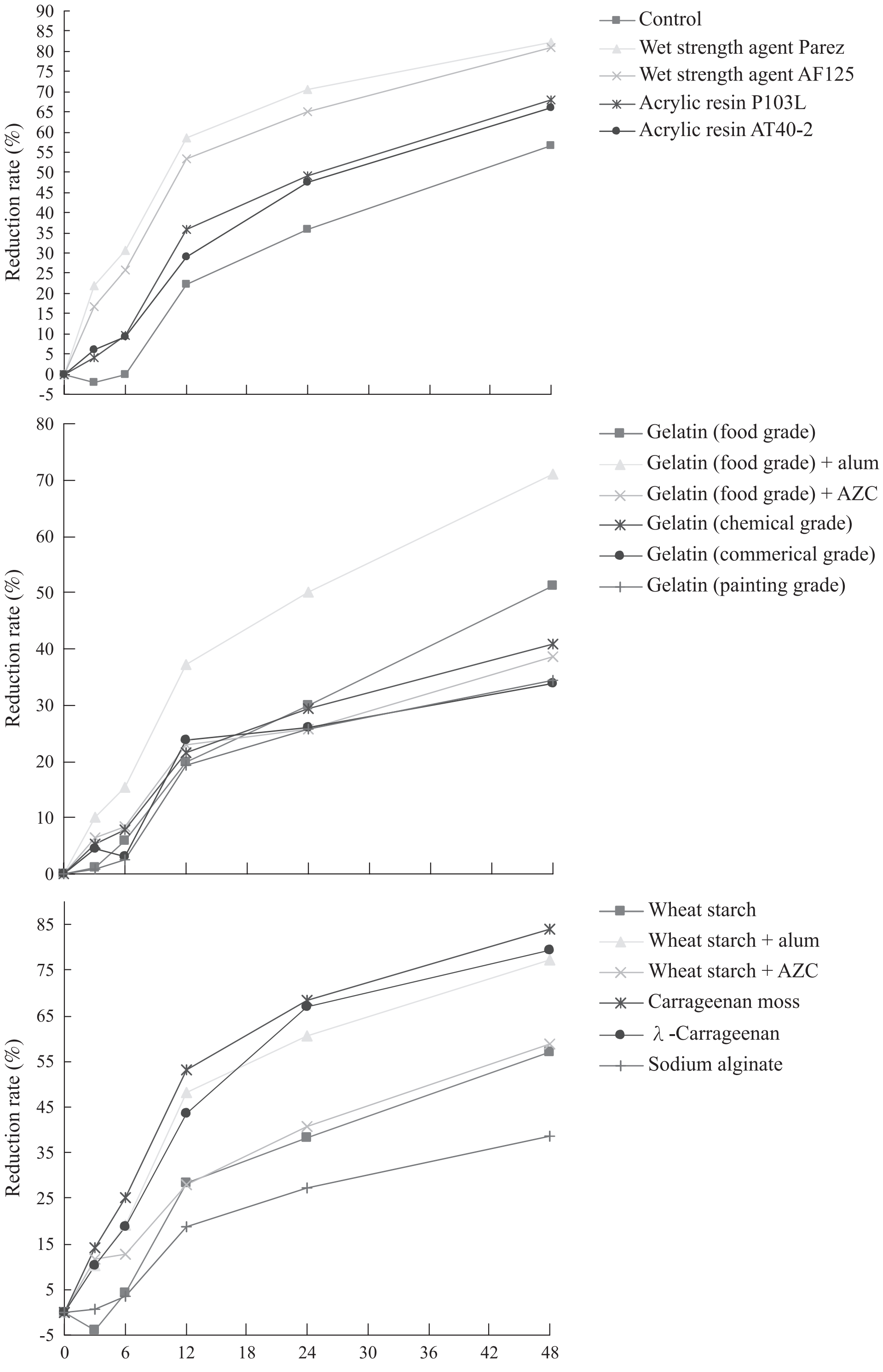

Fig. 1. Effect of 105℃ dry aging on the retention of tear indices of filter paper.

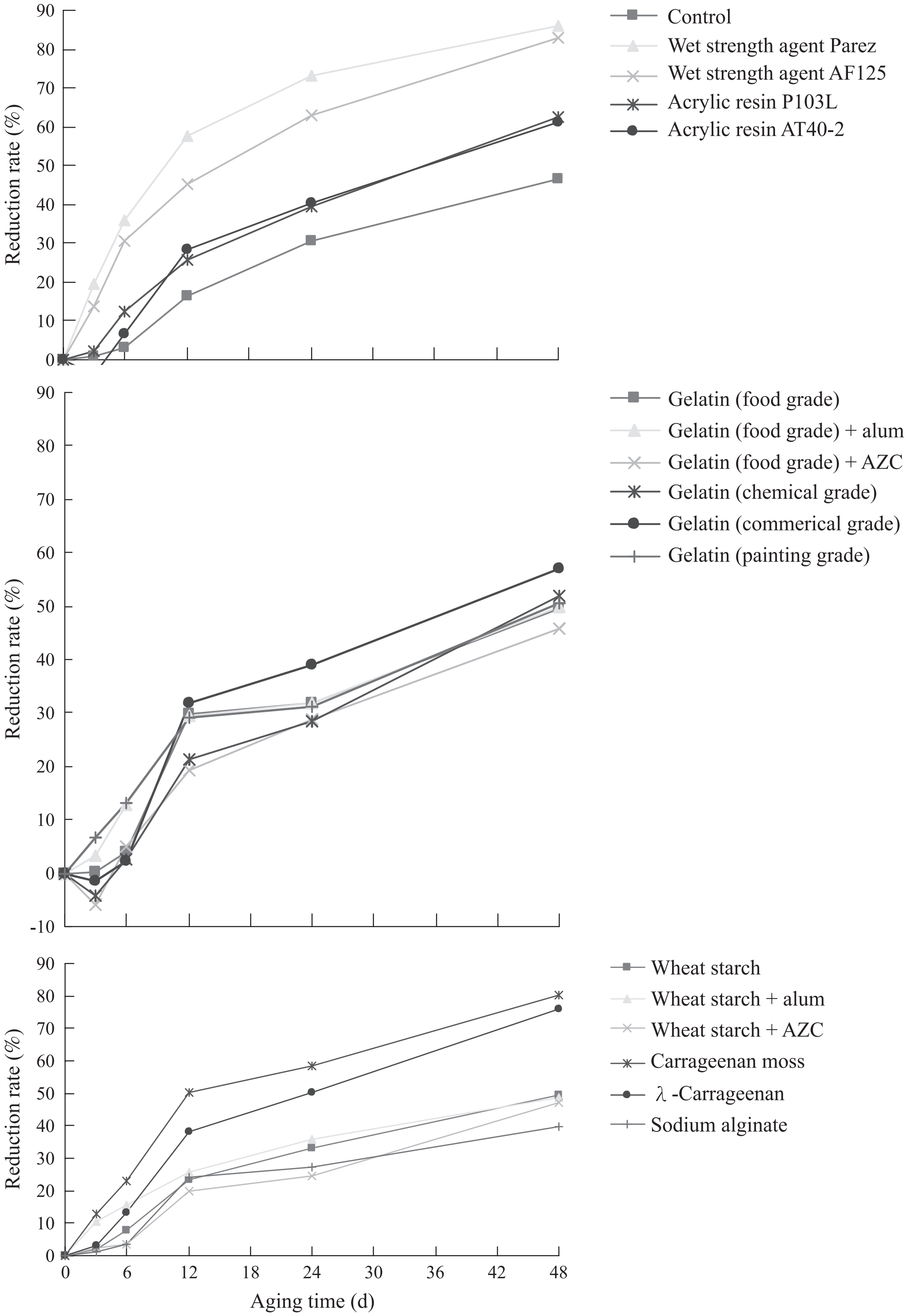

Fig. 2. Effect of 105℃ dry aging on the retention of tear indices of lab-prepared handmade paper.

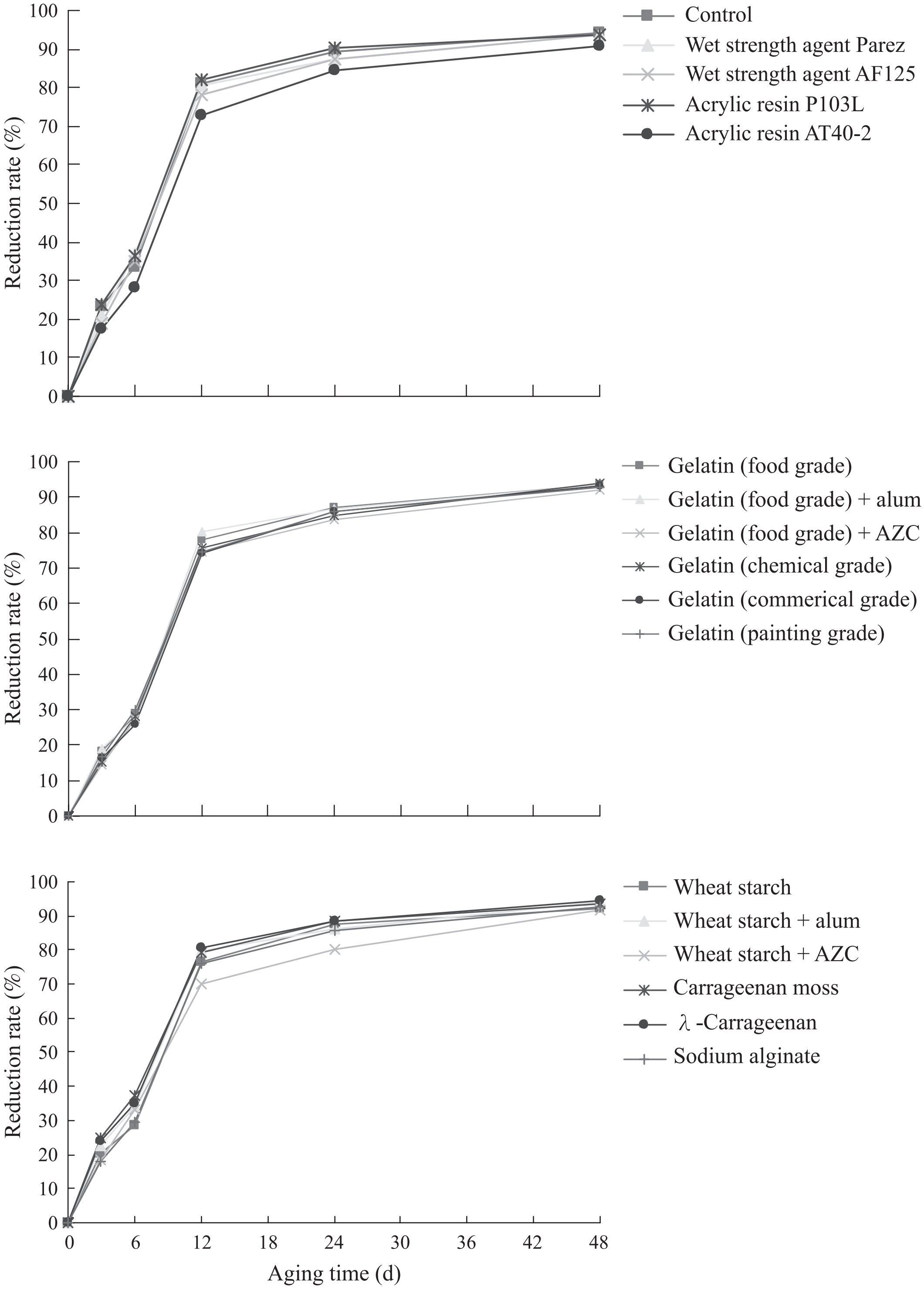

Fig. 3. Effect of 105℃ dry aging on the retention of tear indices of commercial artwork paper.

then subjected to 105℃ dry-heat accelerated aging treatment on tearing strength retention. For the filter paper, when impregnated with gelatins, the retention rate of the food-grade gelatin showed a poorer retained tearing resistance than did the other 3 gelatins (Fig. 1). Traditional impregnating agents are mostly animal glue or starch. Animal glue is also called gelatin, and there are several grades available, such as food-grade, industrial-grade, chemical-grade, painting-grade, etc. The main differences among these are the protein contents, which is highest in the food-grade gelatin, which is derived from fish skin with a protein content of 90%. The painting-grade (commonly called Sasenbon glue) is derived from the inner rawhide and upon boiling extraction is not further purified; hence it has the least amount of protein and often contains impurities such as a minute quantity of fat, etc. Thus, it has adequate insolubilizing properties and flexural toughness, as well as good bonding to fibers. The industrial-grade gelatin contains 82% protein. The chemical-grade gelatin is mainly used in tissue culturing, and has a protein content of 85%. Depending on the culturing purposes, it is often added with various metallic salts. Among the gelatins, the food-grade type is the most widely used, and its solution has the palest coloration. The probable cause is due to its higher viscosity and greater bonding capacity, which causes the impregnated paper to be stiffer, and allows the tearing stress to be concentrated in a smaller area, leading to failure or loss of tear resistance.

However, when 0.05% AZC insolubilizer was also added, the alkaline-buffering effects of the AZC seemed to allow the food-grade gelatin specimen to approach the other gelatins in tearing resistance. Conversely, if alum was used as an insolubilizer, the retention of its tearing resistance was even worse than before. This phenomenon of the pH value of the insolubilizing chemicals causing marked differences became indistinct in the self-prepared handmade sheets containing calcium carbonate (Fig. 2). Furthermore, the phenomenon of inferior food-grade animal glue in the case of the filter paper sample was also absent from our self-prepared handmade sheets. We believe that this may have something to do with the acidic constituents generated during the dry-heat accelerated aging being effectively neutralized by the presence of calcium carbonate, thus retarding the rate of paper degradation. As for the commercial "water-flow" grained handmade paper, although there was some benefit exerted by AZC application on food-grade gelatin treatment (Fig. 3), nevertheless, with an increasing duration of the dry-heat treatment, the various strengths all decreased to near 0, indicating that the original paper properties exerted tremendous influences on the preservability of the paper during aging.

Figures 4~6 show the effects of dry-heat accelerated aging on the pH values of the papers. Upon dry-heat accelerated aging, the papers impregnated with the 2 kinds of wet-strength resins, Parez and AF125, or the 2 carrageenan preparations showed much worse retention of tearing resistance (Figs. 1~3) than did the other resins or adhesives. The aforementioned gelatin cases on the filter paper and self-prepared handmade paper at least had tearing strength retention that was better than or similar to the control. However, for the 2 wet-strength resins and the 2 carrageenan adhesives, the dry heat accelerated aging severely affected their tearing resistance retention. If comparisons were made of aged papers vs. the control (Figs. 4, 6), it was apparent that these resins/adhesives impregnated sheets had relatively lower pH values. In other words, during the aging process, greater

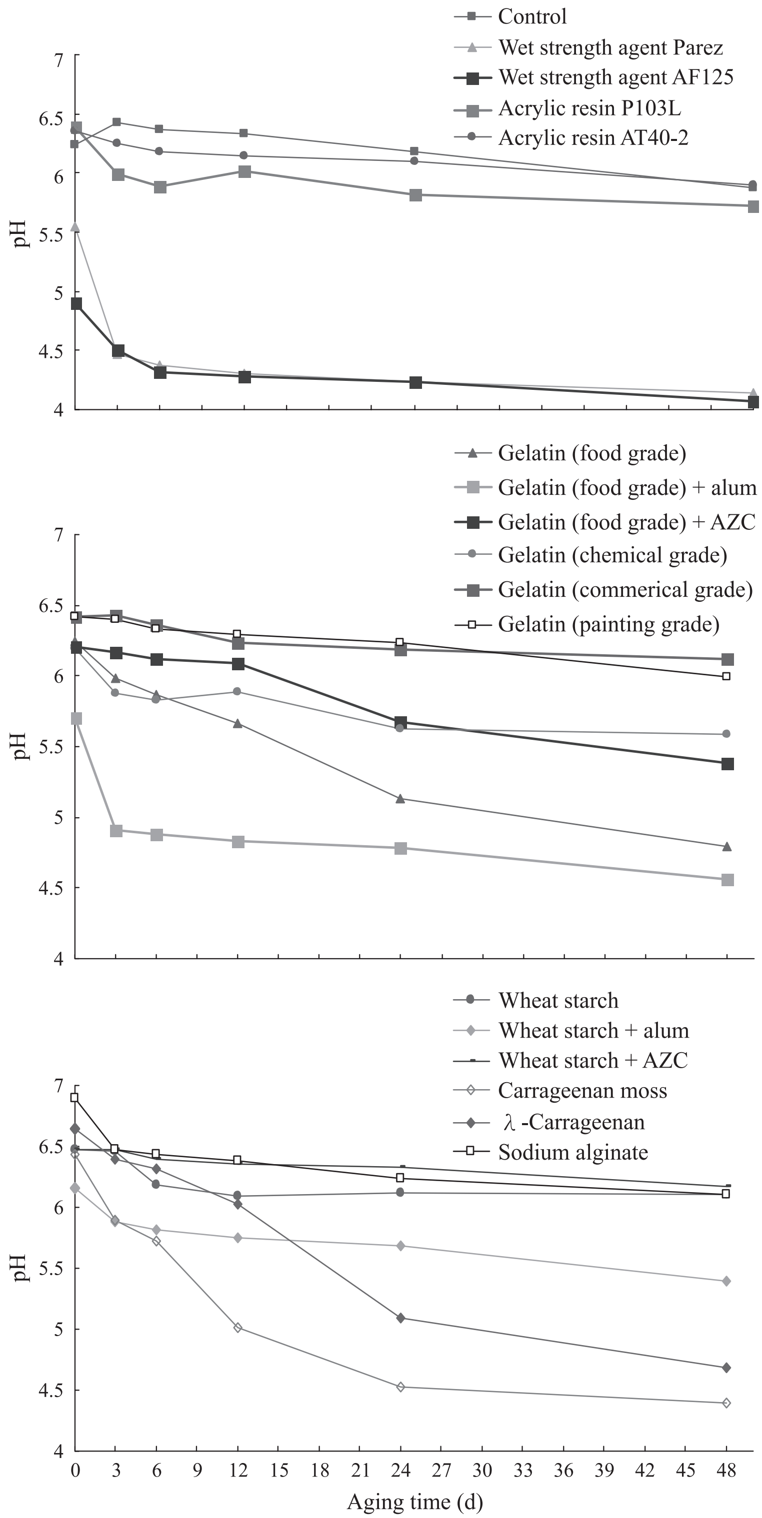

Fig. 4. Effect of dry-heat aging on the pH of filter paper.

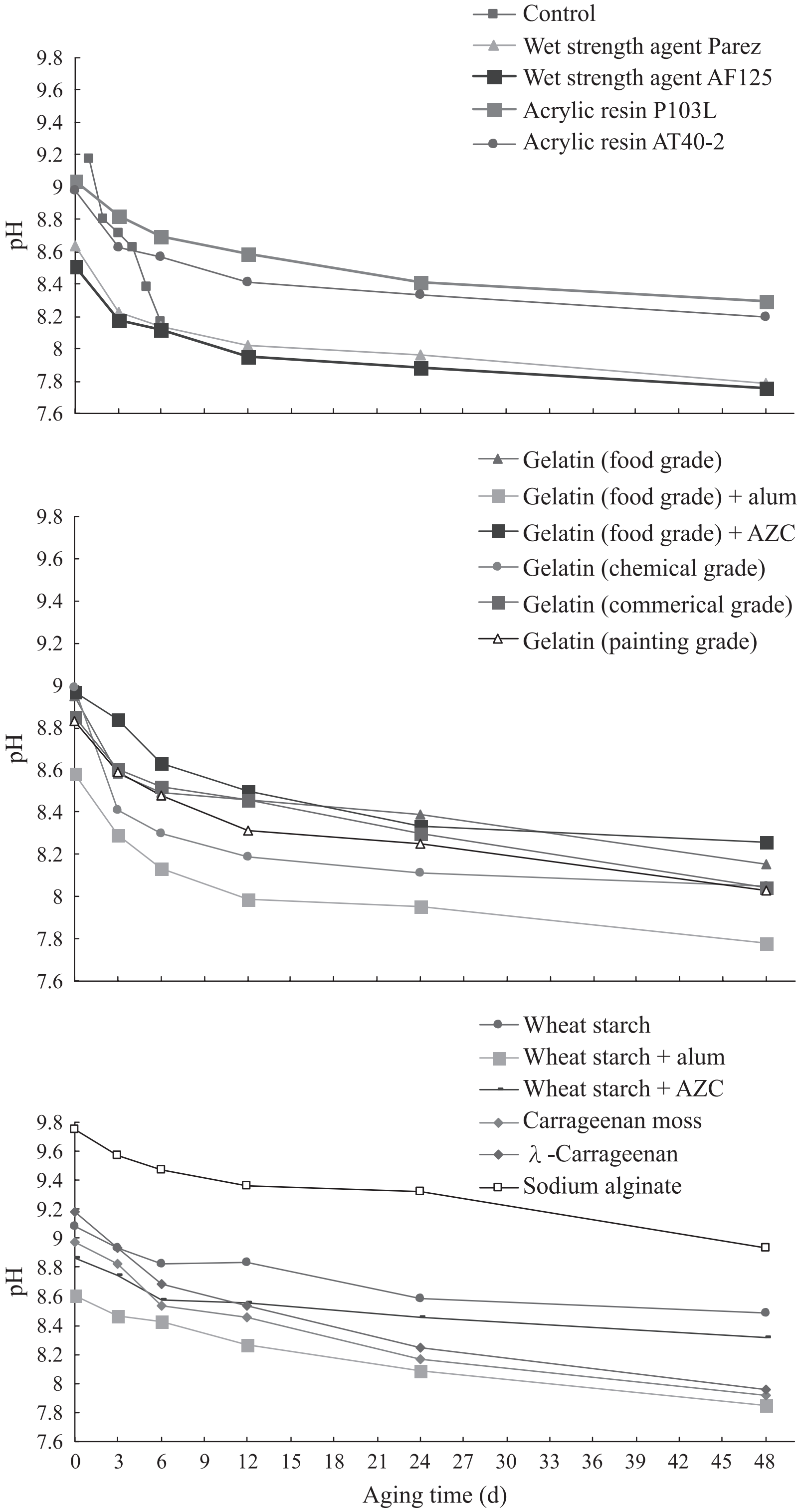

Fig. 5. Effect of dry-heat aging on pH of the lab-prepared handmade paper.

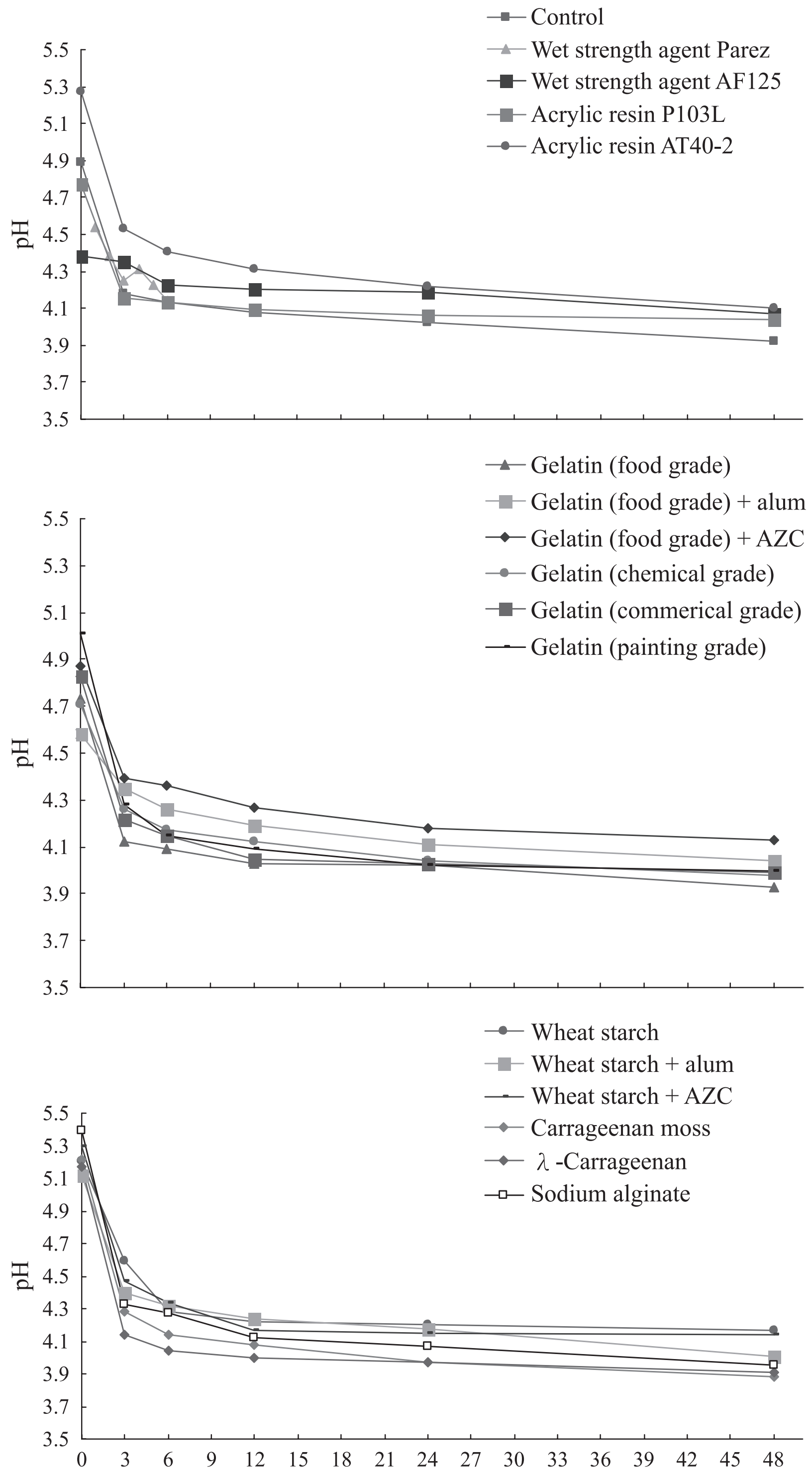

Fig. 6. Effect of dry-heat aging on the pH of commercial artwork paper.

numbers of acidic groups were produced, which naturally fostered faster degradation as a result. The derived acidity is thought to pertain to the chemical compositions of these resins or adhesives. The 2 acrylic resin-treated papers had tearing resistance retentions slightly better than the wet-strength or carrageenan groups, but were inferior to the control and gelatin-treated papers. The longer the dry-heat accelerated aging periods were, the more pronounced the phenomenon became. As for papers impregnated with sodium alginate, after accelerated aging, their tearing resistance retentions were similar to those of the gelatins, and were superior to these of the control and other resins or adhesives. This was particularly notable when the base sheet was filter paper.

Starches and their derivatives are widely used in the paper industry and in mounting artwork as well. In order to smooth the process flow and endow papers with a certain functionality, such as water resistance, serviceability, and even mildew resistance, alum has long been added to gelled starch paste. From Figs. 1 and 2, however, adding 0.05% AZC or alum to the wheat starch created effects upon dry-heat accelerated aging on the retention of tearing strengths that were similar to their actions on gelatin-converted papers. For instance, in our self-prepared handmade paper containing calcium carbonate, the presence of alum did not have much influence. Conversely in the filter paper group, there were significant differences of alum and AZC treatments on the dry-heat degradation resistance. For instance, after 48 d of aging the alum-treated paper retained only one-half the tearing strength of AZC-treated paper. Overall, the starch-impregnated papers had tearing strength retention rates similar to the control and were slightly inferior to those of gelatin-impregnated papers.

Tensile strength

Effects of resin/adhesive impregnation on the aged-paper tensile strength performance of the filter paper are shown in Fig. 7. Among the 3 base sheets for the impregnation treatments, because the thick filter paper was not amenable to the folding endurance test, tensile strength variations in the degradation process were examined instead. Basically, the trends of the resin/adhesive-impregnated filter papers were very similar to those of the tearing strength retentions shown in Fig. 1. The only difference was that the dry-heat accelerated aged samples had a more obtuse response in tensile strength retentions than those of the tearing strength retention. Therefore, we opted to use the more sensitive folding endurance and internal tearing resistance for testing the effects of accelerated aging. We can see that the papers impregnated with gelatins and sodium alginate compared more favorably in tensile performances than other resins or adhesives. Similarly, using AZC to replace alum appeared to be a wise choice.

Folding endurance

Effects of accelerated aging of the various resin/adhesive impregnated lab-prepared handmade papers and commercial papers on their folding endurance are respectively shown in Figs. 8 and 9. The 2 figures show that all adhesive-impregnated papers had greater folding strength than the base papers. The degree of enhancement, however, enormously differed among the applied adhesives, with gelatin treatments imparting the greatest enhancements, and starch ones the least. Gelatin treatment is thought to endow the paper with flexural toughness as it forms proteinaceous films over the base sheets. The Sasenbon gelatin used in painting provided a lesser boost to folding than did the other gelatins; however, because of its higher fat

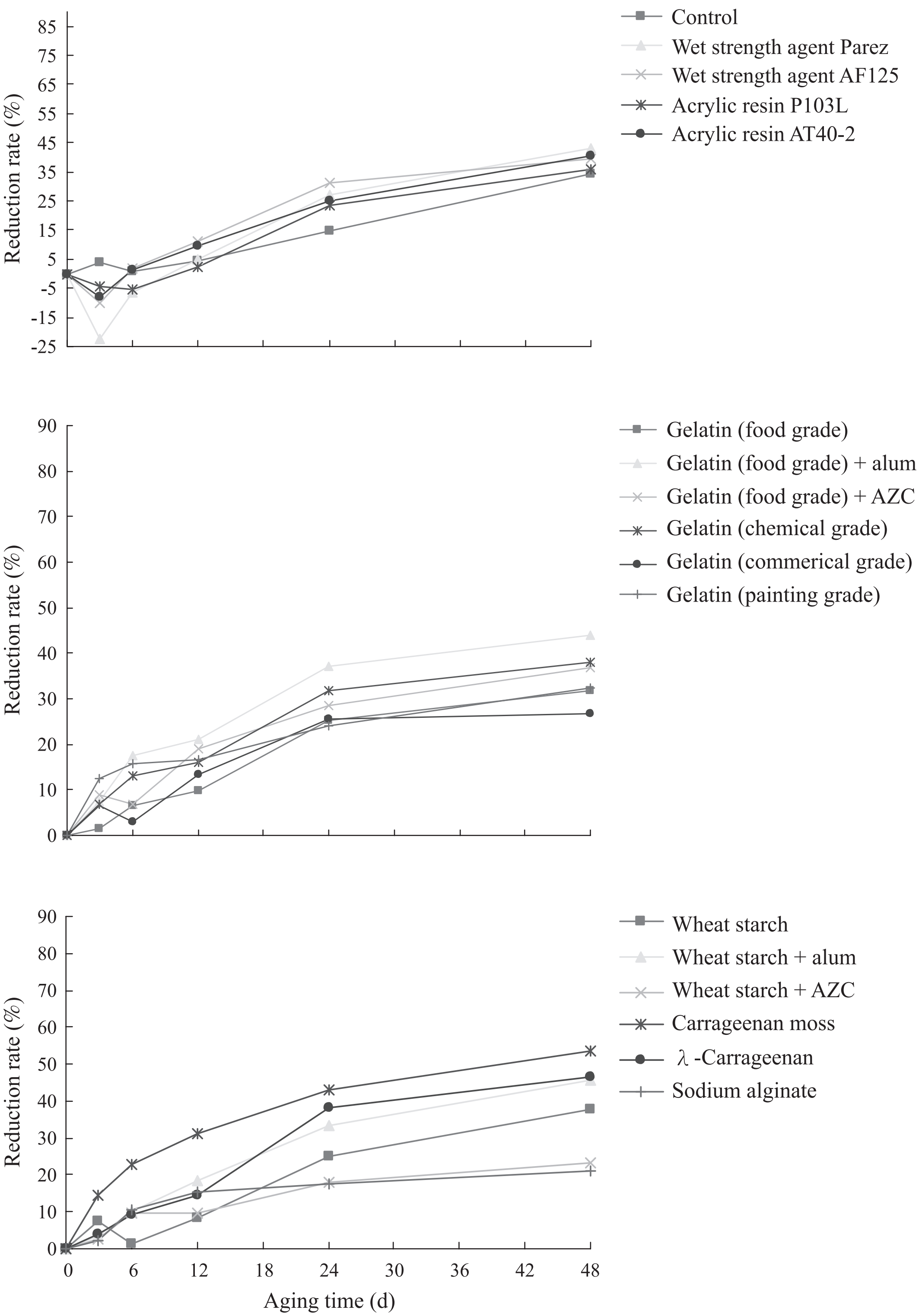

Fig. 7. Effect of 105℃ dry aging on the retention of tensile indices of filter paper.

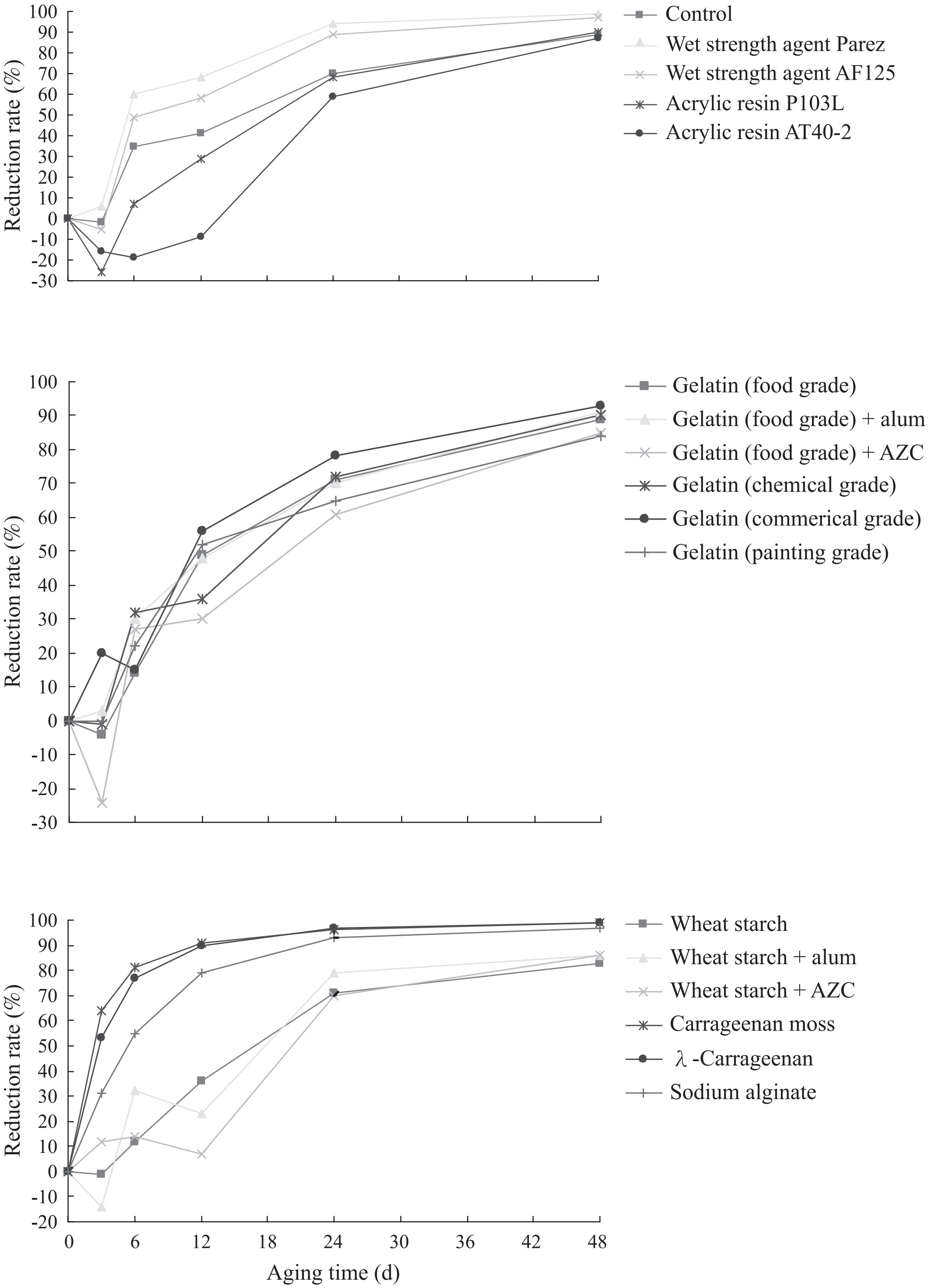

Fig. 8. Effect of 105℃ dry aging on the retention of folding endurance of lab-prepared handmade paper.

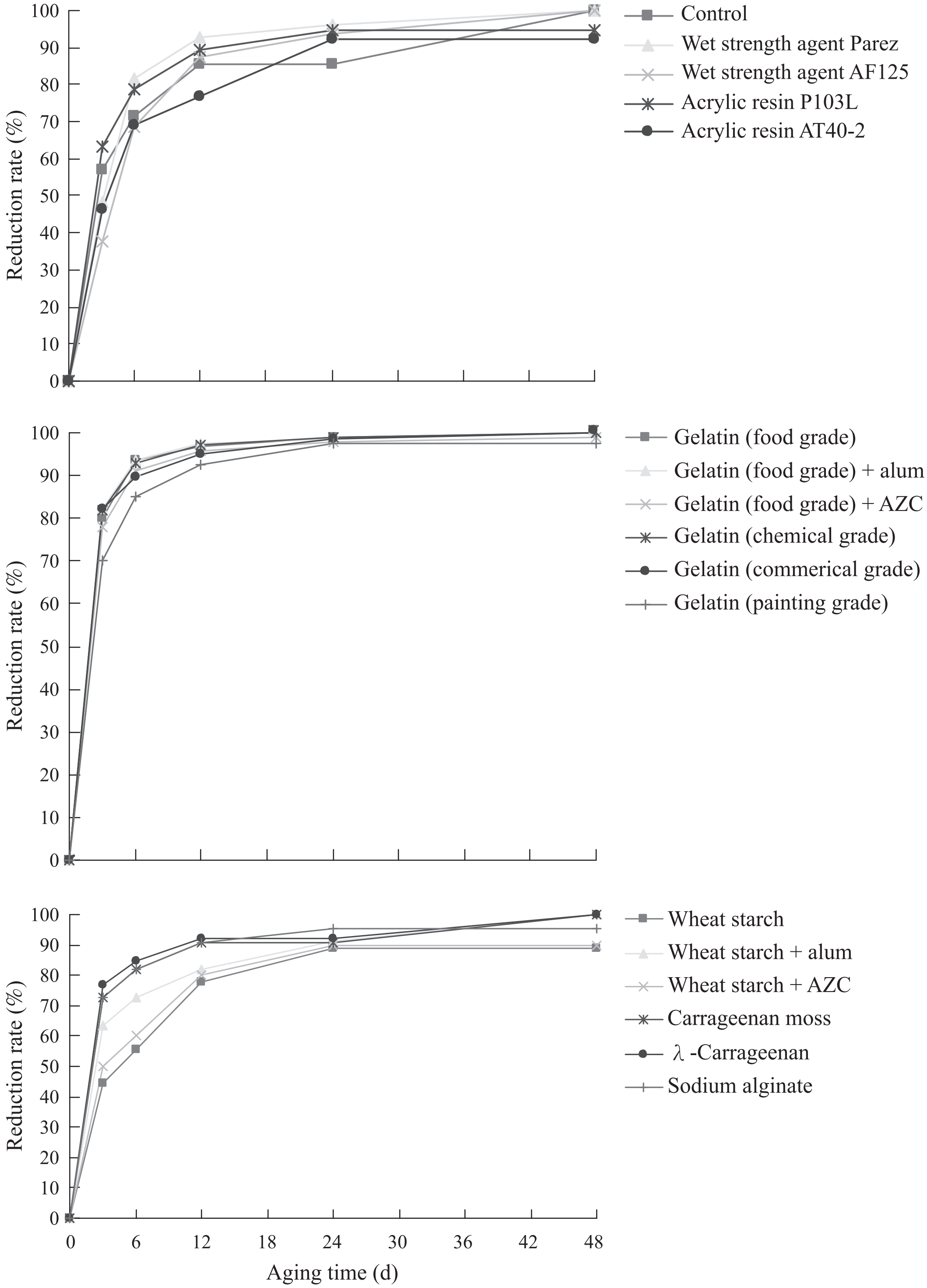

Fig. 9. Effect of 105℃ dry aging on retention of folding endurance of commercial artwork paper.

and impurity contents, it was well-retained in the papers. The starch-treated papers, on the other hand, were less likely to form a film, and tended to impart a more rigid and frail bonds, hence the least amounts of folding enhancements. Despite a poor folding enhancing efficacy, starches were more resistant to high temperatures, hence the starch-treated paper tended to retain the property better upon aging. Furthermore, regardless of whether alum or AZC was used, starch retention remained stable. Carrageenan and λ-carrageenan are plant proteins, which imparted similar folding enhancement results as those of the starch ones, and were inferior to the gelatins. They also had poorer folding retention than starches, probably due to their poorer heat resistivity. Because acrylic resins are acidic to begin with, and the films they formed were less flexible than those of gelatins, they had poor folding strength retention after aging. After 48 d of aging, the folding often fell to 3% or less. Based on these results, users of acrylic resins and wet-strength resins must bear in mind that these additives are not conducive to the preservation of paper. With respect to the commercial “water-grained” artwork paper, regardless what kind of resins or adhesive it was impregnated with, only at an early stage of the dry-heat treatment that the folding-enhancing quality of the additives could be discerned. Along with advancing aging, however, all folding retention levels eventually became 0. The main cause of the failure was that the intrinsic materials used in making the paper and the alum used in its sizing led to an acidic nature of the paper. These results provide a cautionary note to users of this paper that their artwork might not last.

Paper brightness

Figures 10~12 show the effects of dry-heat aging on the brightness of various resin- and adhesive-treated papers. Figures 13~15 present color differences, or ΔE* values, of impregnated papers after dry-heat aging. The paper brightness and color difference (the ΔE* value) of the aged filter paper showed a similar trend as those of strength retention. Paper brightness values of the gelatin group after the accelerated aging were very close to that of the control. Together with wheat starch, they tended to perform well in brightness retention. If alum was added to them, however, there was a serious impact on the brightness retentions and color difference values. When replacing alum with AZC, on the other hand, the retained brightness was superior even to any treatment without adding an insolubilizer. The same also applied to the commercial “water-flow” grained paper. As for the self-prepared, calcium carbonate-containing handmade paper, the addition of either alum or AZC had no discernible effect on their brightness and color difference values. Among the various resins and adhesives, the ones showing the greatest impact on the brightness performance were carrageenans, irrespective of the paper substrates. For resin/adhesive impregnated self-prepared handmade papers, the post-aging degraded paper mostly had brightness retention levels inferior or only similar to that of the control. For the commercial “water-flow” grained paper, however, except for the cases of carrageenans, all resin and adhesive treatments tended to enhance the brightness retentions after aging. Thus, strictly speaking, the materials and methods of processing of such papers rendered it an unsuitable medium for artistic creations.

CONCLUSIONS

From the experimental results, we have surmised the following conclusions. The in-

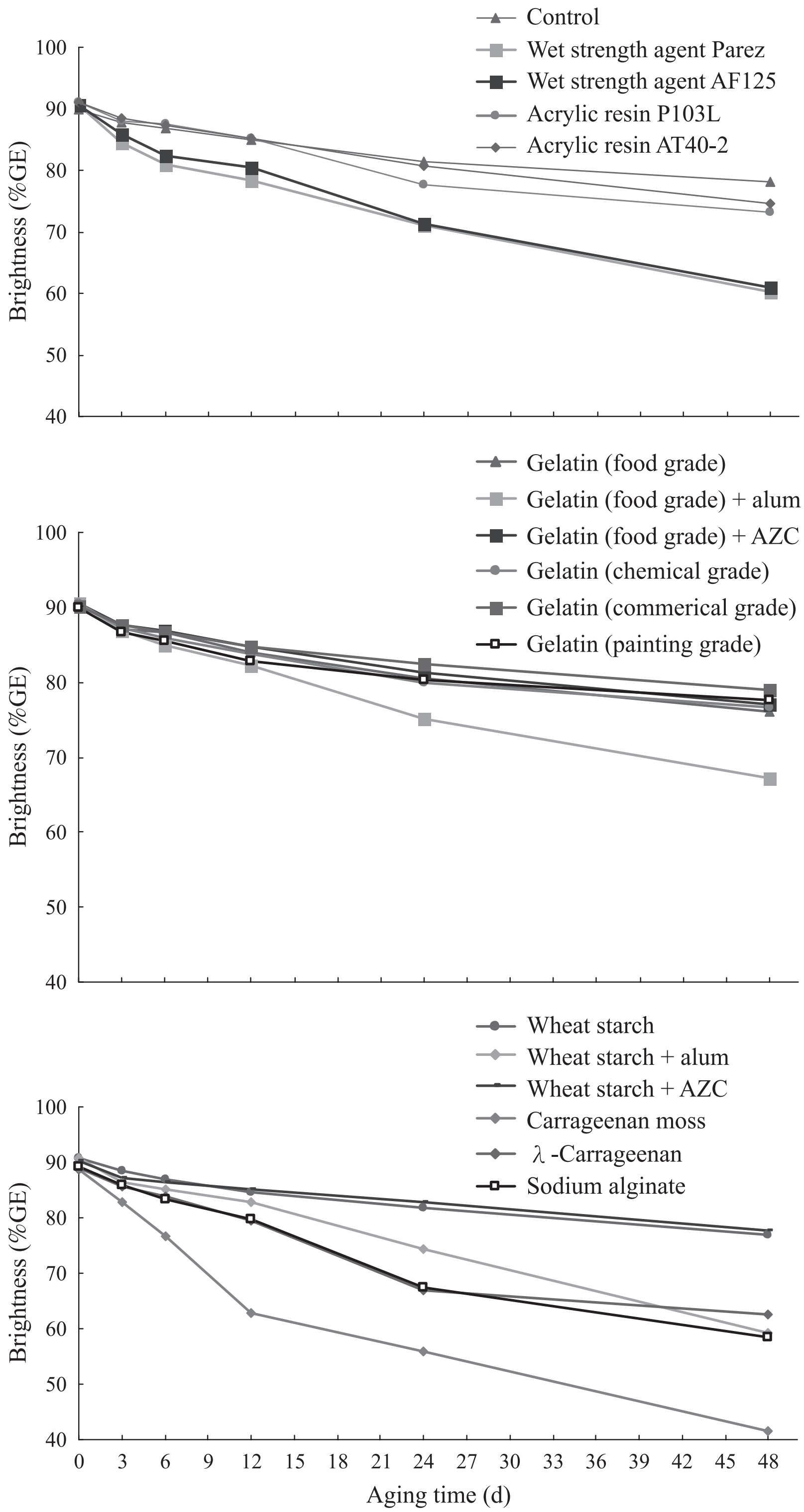

Fig. 10. Effect of dry-heat aging on the brightness of filter paper.

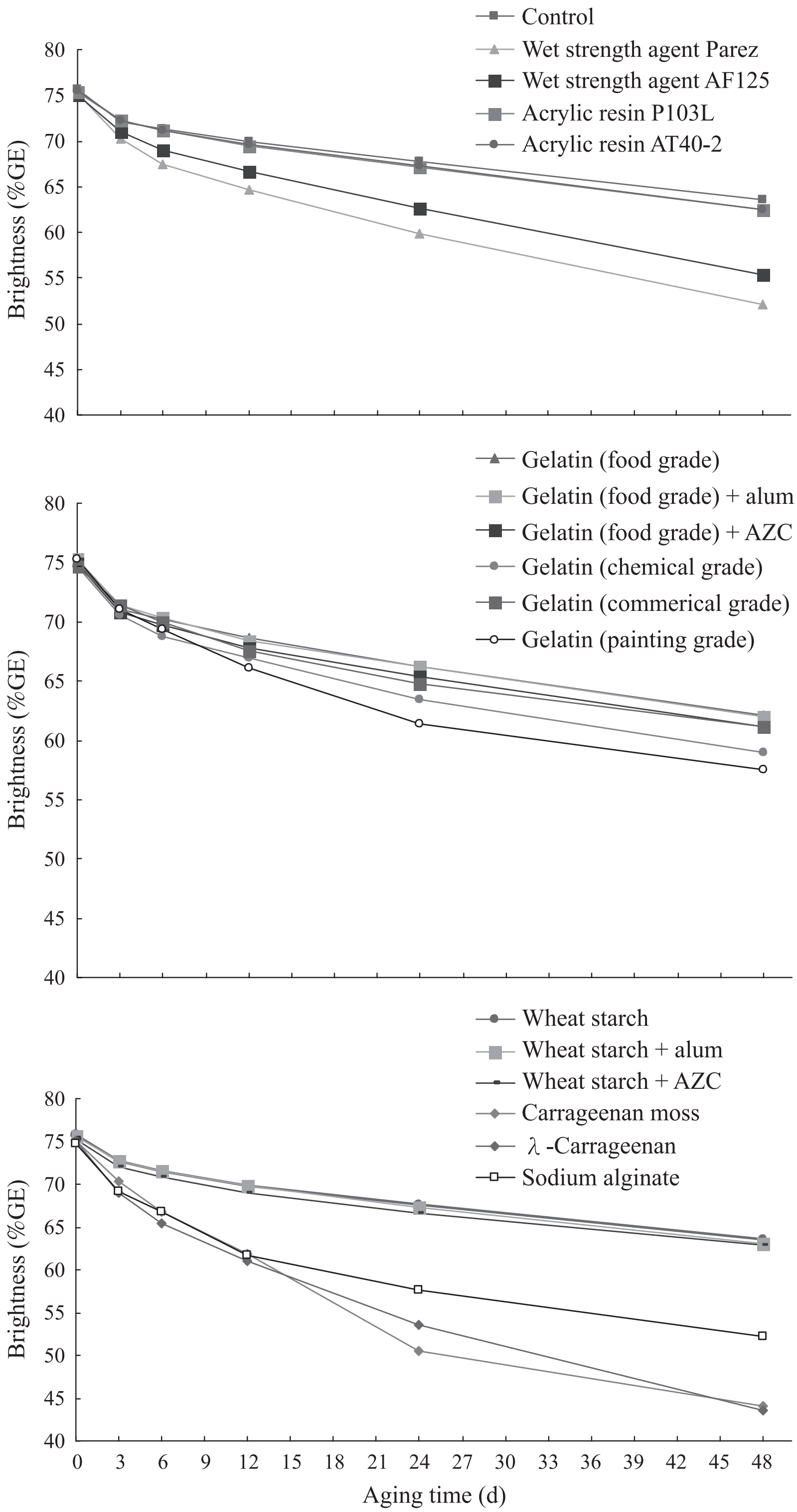

Fig. 11. Effect of dry-heat aging on the brightness of lab-prepared handmade paper.

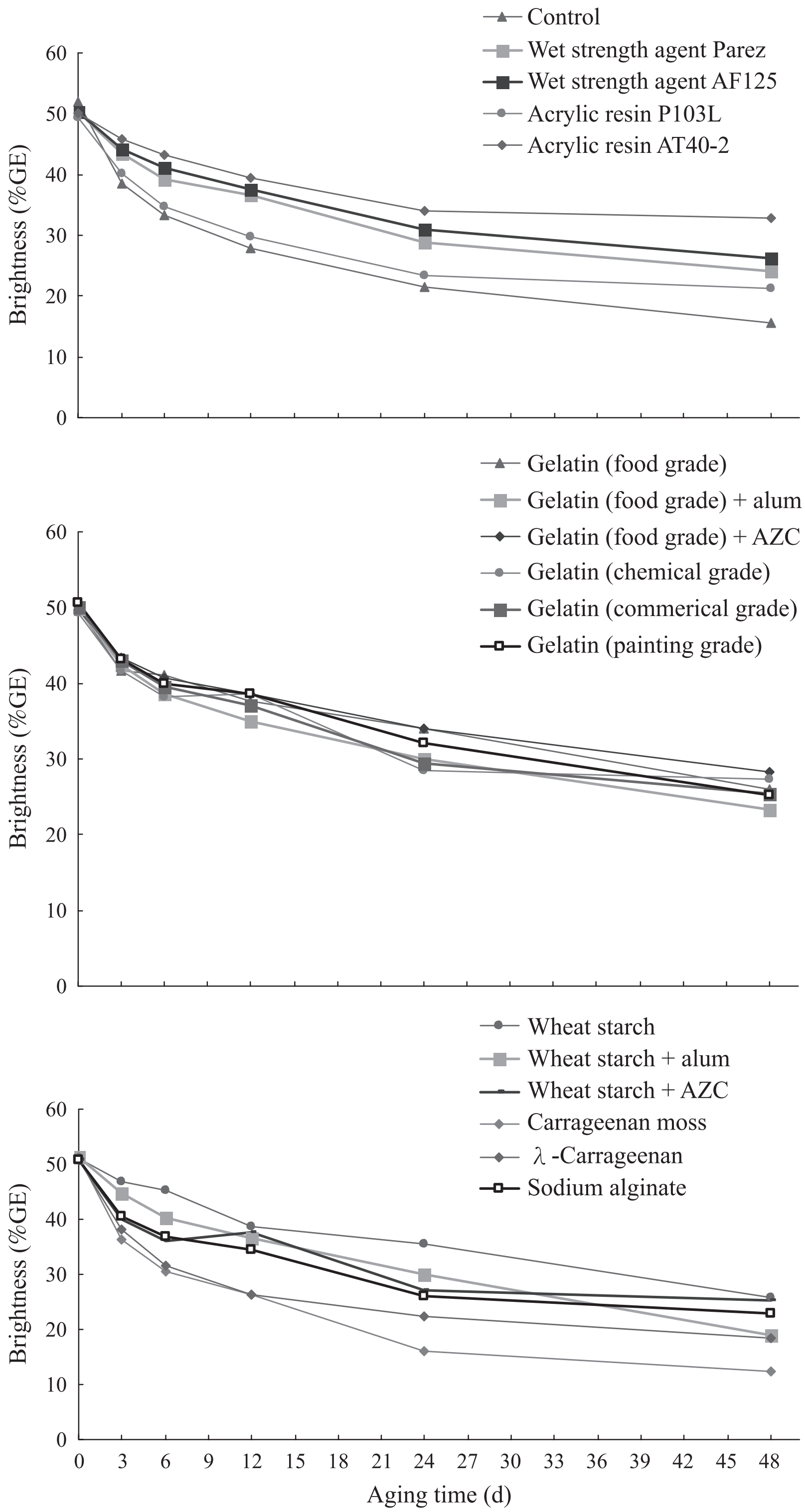

Fig. 12. Effect of dry-heat aging on the brightness of commercial artwork paper.

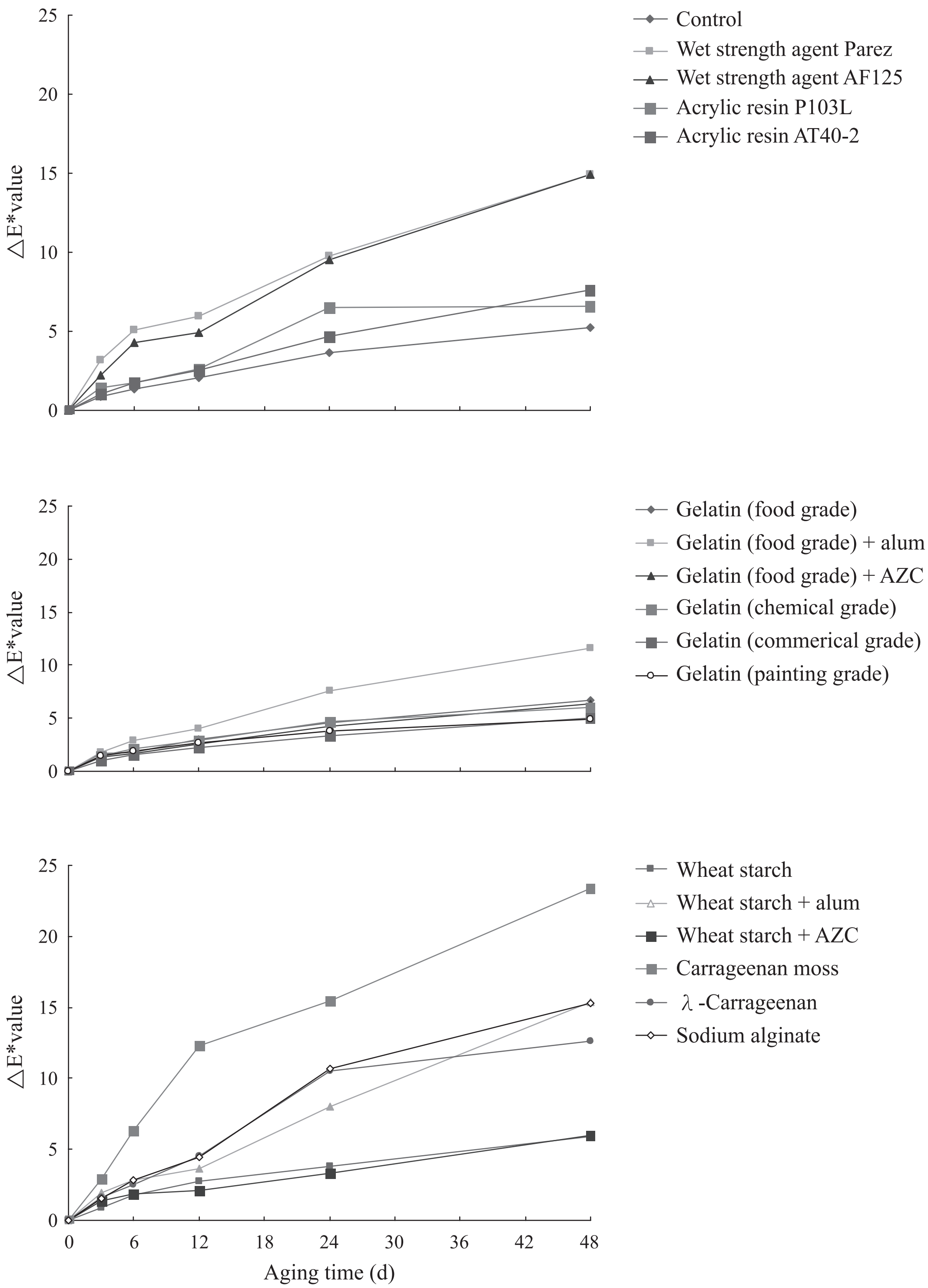

Fig. 13. Effects of different resin/adhesive additives and dry-heat aging time on the ΔE* value of filter paper.

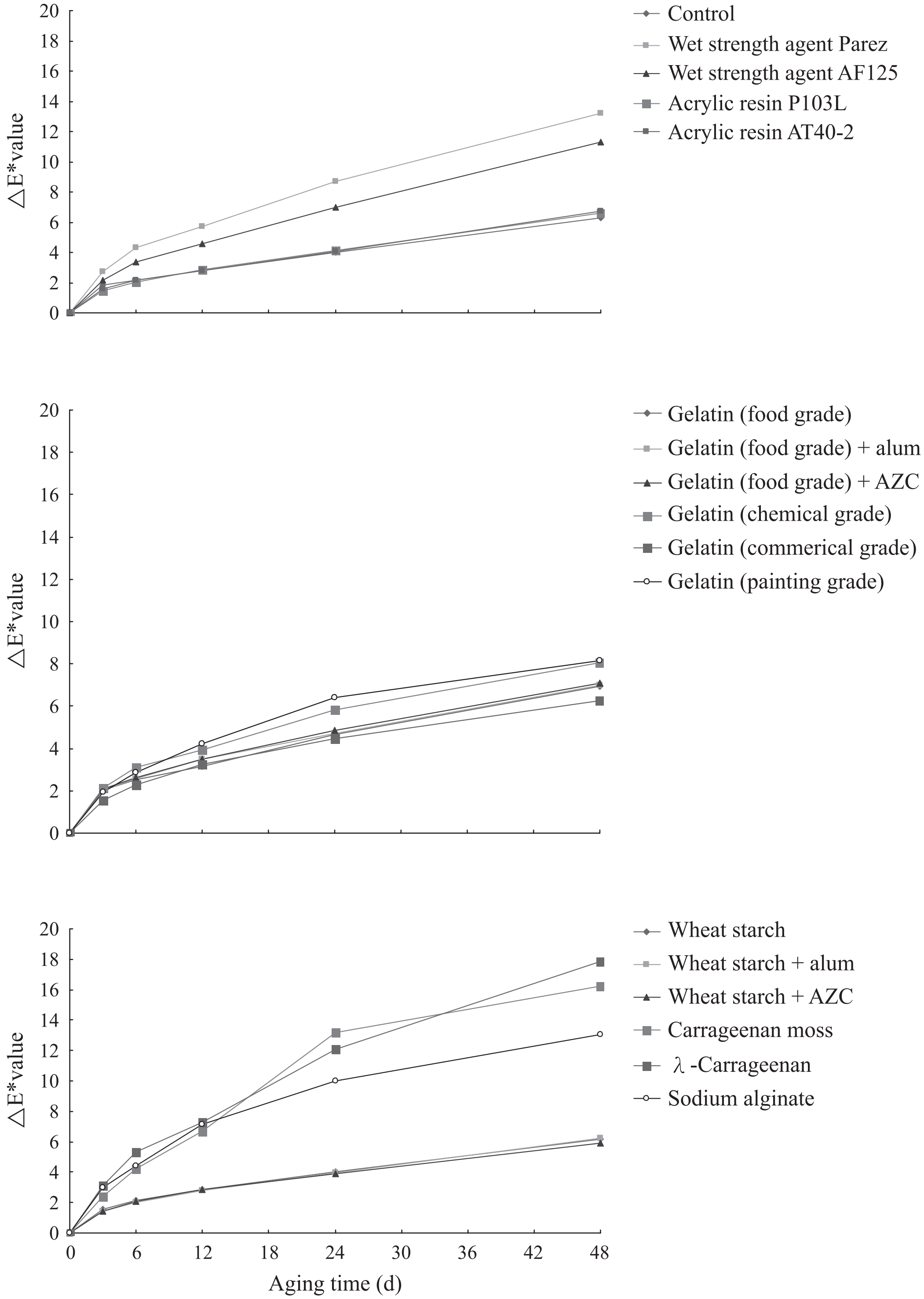

Fig. 14. Effects of different resin/adhesive additives and dry-heat aging time on the ΔE* value of lab-prepared handmade paper.

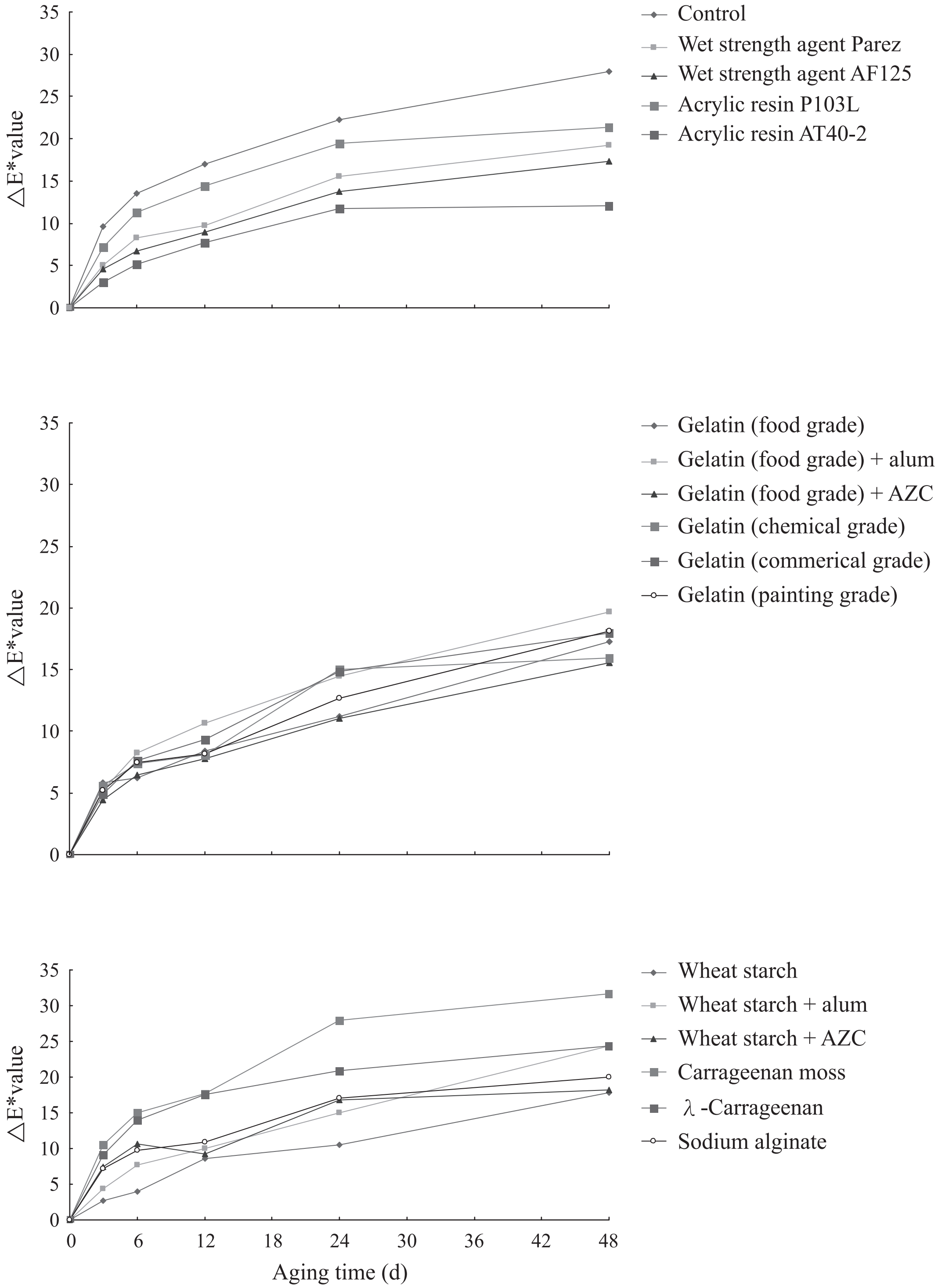

Fig. 15. Effects of different resin/adhesive additives and dry-heat aging time on the ΔE* value of commercial artwork paper.

trinsic nature of the papers greatly affected their preservation. Although the original folding endurance of the commercial “water-flow” grained paper could be markedly boosted by impregnating it with animal glues, upon dry-heat aging degradation, the strength retentions were very poor, and incapable of long term preservation. If such paper was selected as the medium of calligraphic and painting works, the risk of them disintegrating over time is high. Individual resins or adhesives exerted different effects on the treated paper. They not only affected the original strengths of the paper, but performed differently upon dry-heat accelerated aging treatment. Their influences on color changes of the aged paper were similarly notable. Taking the tearing strength retentions, for instance, values after dry-heat aging of the 2 kinds of wet strength resins, carrageenans, and animal glues with the addition of alum were relatively low. When an insolubilizing agent was added to the resin or adhesive impregnated papers, AZC was a much better choice than alum. This phenomenon was more pronounced in the filter paper than in the self-prepared handmade paper, mainly because there was no calcium carbonate in the former to buffer the acidity of the alum.

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