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Modification of hydrogenated Bisphenol A epoxy adhesives using nanomaterials

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ABSTRACT

Color-stable hydrogenated Bisphenol A (HBA) epoxy adhesives, containing organic–inorganic hybrid nanomaterials, were prepared and their properties investigated. Poly(propylene glycol)bis(2-aminopropyl ether) (D230) was used as the room temperature curing agent, and functional organic–inorganic hybrid nanomaterials, to tailor the adhesives, were prepared by a sol–gel reaction of 3-glycidoxypropyltrimethoxysilane and tetraethoxysilane. The commercial polyhedral oligomeric silsesquioxanes (POSS) having epoxy functional groups were also used. The concentration dependence of different nanomaterials, containing epoxy functional group for HBA/D230 adhesives, was studied. The tensile strength increased with the addition of nanomaterials having glycidyl epoxy group; however, the dependence varied with the size, the number of functional groups, and the amount of the addition. HBA/D230 adhesives containing different amounts of nanomaterials, whose compositions are similar to that of granite, were applied to the Korean granite and the results were compared with those obtained by using commercial adhesives, which have the problem of significant color change and high viscosity. The mechanical properties of HBA/D230 adhesives, containing POSS having glycidyl epoxy group, are found to be similar to those of commercial adhesives. Besides, it has low viscosity and long-term color stability.

1. Introduction

Epoxy resins based on Bisphenol A are one of the most important thermosetting materials that are widely used as adhesives because of their excellent thermal, mechanical and electrical properties [1]. One important application of these adhesives is for the conservation of stone monuments by restoring their strength, which is severely weakened by decay or accident.

Historical stone monuments, particularly those in the open air, are generally vulnerable to irreparable damage owing to the degrading effects of natural weathering and air pollution. For conserving such monuments, the choice of the right adhesive becomes a key factor. For conserving Korean stone monuments, the commercial AW106-HV953U adhesive (Ciba-Geigy Ltd.) was used. However, its properties were never compromised as they should suit the characteristics of the decayed stone of the Korean historical monuments, which vary widely with the cause and degree of decay. If treatment is carried out without adequate knowledge of the properties of the adhesives and the characteristics of the decayed stone system, or, without proper optimization of the molecular structure for conservation purposes, it will eventually lead to additional decay phenomena, such as detachment and scaling [2,3]. Therefore, it is imperative that one thoroughly understands the properties of adhesive material and also the stone characteristics of the monuments, before choosing the conservation materials. In addition, the mechanical strength of the adhesive and the way it is applied are also important. If the strength is too strong, or if the application is only on the surface of the decayed stone, the adhesive may lead to further deterioration [4].

The commercial AW106-HV953U adhesive widely used for stone conservation, including the stone monuments in Korea, is based on Bisphenol A epoxy resin. It is highly viscous and yellowish with undesirably strong mechanical strength. Its high viscosity prevents the adhesive from penetrating into the decayed Korean granite of the monument and its greater strength in relation to that of the decayed stone, leads to secondary detachment with time. Another negative aspect of this adhesive is its high thermal expansion coefficient, which promotes the decaying process under humid conditions of seasonal outdoor temperature changes.

Long-term color stability can be obtained by hydrogenation of the unsaturated bonds of the epoxy resins based on Bisphenol A. Although hydrogenated Bisphenol A (HBA) epoxy resin is the right

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adhesive for stone monuments from the point of view of color stability, it has the drawback of low mechanical strength than that of Bisphenol A epoxy resin having unsaturated bond in main chain.

For improving the strength of these resins, organic–inorganic hybrid materials were chosen as additives. Nano-sized organic–inorganic hybrid materials are considered to be high-performance materials, because they have larger surface area, and hence any small changes in nanoparticles may cause significant changes in the nanostructure and consequently in the macroscopic properties too [5]. Polyhedral oligomeric silsesquioxanes (POSS) are inorganic silica-like nanocages having organic substituents. The reactive group, which takes part in the formation of the hybrid nanocomposite, is placed in the organic chains. They are used as multifunctional polymer additives, acting simultaneously as molecular level reinforcements, processing aids, and flame retardants [6–12]. We chose POSS in HBA to improve the mechanical strength, because the composition of POSS is similar to that of granite. In addition, POSSs may possibly remove the condensed moisture inside the stone monument, especially those located in the open air, because the POSS resembles a nanosized particle of SiO_2 having well defined voids, through which small molecules such as water vapor can be transported [10]. As deterioration of the stone monument is caused mainly by water, the best way to prevent deterioration is to prevent water from penetrating into the stone, and to allow the water vapor inside the stone to move out. The POSS provides the required room for water vapor to evaporate easily unlike the adhesives having dense configuration.

The present study is aimed at developing HBA epoxy resin-based adhesives, which impart improved properties as compared to those of the existing commercial products, based on Bisphenol A epoxy resin such as AW106-HV953U (or AY103-HY956) adhesive. The focus has been mainly on ensuring good penetration and appropriate mechanical strength. Poly(propylene glycol)bis(2-aminopropyl ether) (D230) was used as the room temperature curing agent in this study because of the low viscosity of the epoxy/D230 system. Nano-materials having flexible segments were prepared and compared with the commercial POSSs. To evaluate the suitability of the new materials for use in stone conservation, their viscosity, thermal coefficient and mechanical strength were evaluated.

2. Experimental

2.1. Materials

The hydrogenated diglycidylether of Bisphenol A (HBA) epoxy resin and poly(propylene glycol) bis(2-aminopropyl ether) (D230, M_w=230) were obtained from Kukdo Co. Ltd. (Korea) and used as-received. The molecular weight of HBA is ca. 460 g/mol, and the epoxy equivalent weight is 230 g/mol. A red dye (Hyundai Chemical, DyeRed 33) was used for visual observation. Epoxycyclohexyl POSS (EP0408, M_w=1772.73) and glycidyl POSS (EP0409, M_w=1337.33) were purchased from Hybrid Plastics and used as-received. The number of epoxy groups was 10 for EP0408 and 8 for EP0409.

Tetraethoxysilane (TEOS, 99%) and (3-glycidoxypropyl)trimethoxysilane (GPTMS, <98%) were purchased from Sigma–Aldrich Co. Inc. Methanol and HCl (37 wt% in water, 99.999%) were purchased from Aldrich and used as solvent and catalyst, respectively, for the sol–gel reaction of the polysiloxane nanometerials. The chemical structures of HBA, D230 and POSSs are shown in Scheme 1.

Commercial adhesives used for conservation (AY103-HY956 and AW106-HY953U; Ciba-Geigy Ltd.) were used as-received. Granite samples from Namsan, Korea, were cut into $25 \times 10 \times 30$ mm^3 blocks, rinsed with deionized (DI) water for an hour by ultrasonic agitation and dried in an oven at 150 °C for a week. Removal of residual water was confirmed by the constant weight.

2.2. Preparation methods

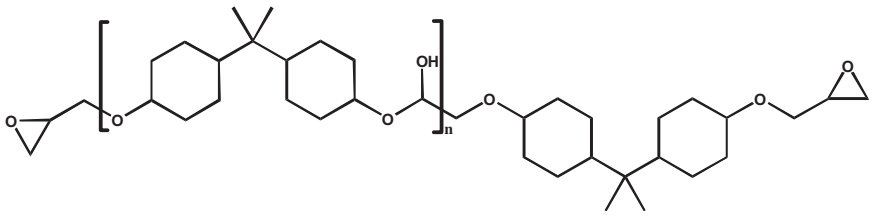
Polysiloxane having glycidoxypropyl groups (PS) for this study was prepared [13]. TEOS was hydrolyzed in DI water for 18 h at 22 °C in the presence of 0.08 wt% HCl catalyst (the mole ratio of TEOS:water=1:10). PS was prepared by the reaction of 0.02:99.98 weight ratio of hydrolyzed TEOS:GPTMS for 3 days at 22 °C under 0.08 wt% of HCl catalyst. PS was purified using dialysis membrane (cut off: 1000, Spectrum Laboratories Inc.) and dried in vacuum oven at 35 °C for a month before the preparation of adhesives. The average molecular weight of PS prepared was ca. 4500 g/mol, as estimated by GPC using polystyrene standard. The synthesis method and characterization were reported earlier in this laboratory [13].

Different amounts of nanomaterials (10, 20 and 30 wt% of POSSs and 3, 5 and 7 wt% of PSs) were added to HBA and stirred using a mechanical stirrer (600 rpm). To this was added the curing agent to form a homogeneous mixture by stirring for 5 min with the mechanical stirrer (600 rpm). Air was removed in vacuum oven for 10 min and then the sample was prepared by immediately pouring the solution into a silicon mold to characterize the properties. The reaction was checked at room temperature by FT-IR measurement.

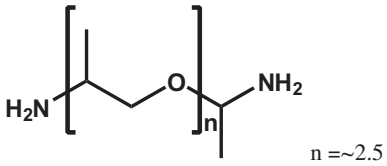
2.3. Characterization

Nuclear magnetic resonance (NMR) spectra were recorded by a Varian Unity-plus 300 spectrometer. The viscosity of the solution was measured with a vibro viscometer using sine-wave vibro viscometer SV-10 (A&D Co. Ltd.) at 28 °C. To determine the curing time, Fourier-transform infrared (FT-IR) spectra of the sample were measured with a Perkin Elmer, Spectrum 100 instrument equipped with attenuated total reflectance (ATR). A total of 128 scans were obtained with a resolution of 4 cm^{-1}. The cross-section of the samples fractured in liquid nitrogen were measured with a HITACHI S-4200 field emission scanning electron microscope (FE-SEM) equipped with energy-dispersive X-ray spectroscope (EDX). The thermal stability of the samples was determined by differential scanning calorimetry (DSC, TA Instruments Ltd., 2010 DSC) in the temperature range of −50 to 200 °C at a scanning rate 10 °C/min.

The sample for the tensile lap-shear strength (ISO 4587) was evaluated using stainless bars treated with sandpaper no 60 and the values were measured using a Universal Testing Machine (DTU-900MH30kN, Daekyung Teck) at a cross-head speed of 2 mm/min. The compressive shear strength of the adhesive (KS M 3721) treated on granites was measured by Universal Testing Machine; the sample size was $25 \times 10 \times 30$ mm^3 and the adhesive test area was 25×25 mm^2. The characterization of the stone was conducted by stereomicrophotographs (Nikon SMZ1500). Wide-angle X-ray diffraction analysis (XRD) was conducted with a Rigaku, D/MAX RINT 2000 high resolution diffractometer employing Ni-filtered CuKα radiation. Dried samples were mounted on an aluminum sample holder, and the scanning angle was changed from 4° to 60° at a scanning rate of 5°/min. All spectra were measured at ambient temperature. The porosity and pore size were determined by the Hg porosimeter (Autopore IV 9500, Micromeritics Co.) at 50 μmHg (5 min). The adhesives containing red dye were used to monitor the penetration inside the stone samples. The average penetration depth using red dye was measured by image analysis after measuring the cross-section of the sample by stereomicrophotography [14] under the assumption that the adhesives penetrated as deep as the red dye did. Thermal expansion coefficient was measured by dilatometer (NETZSCH DIL 402 C). Preparation of sample condition was based on DIN 51045, DIN 52328 and DIN 53752, and the length of the sample

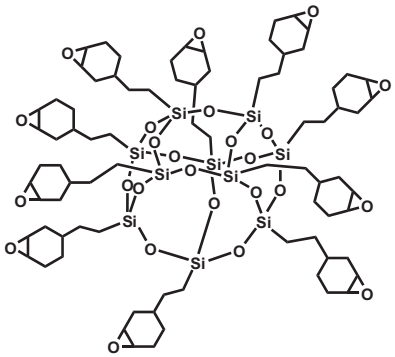


Hydrogenated-Bisphenol-A (HBA)

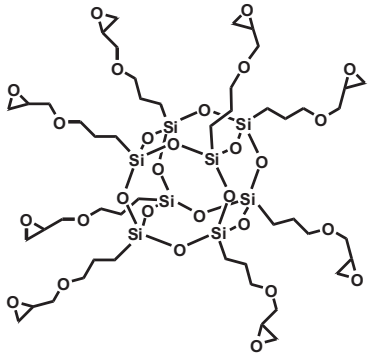


n =~2.5

Poly(propylene glycol) bis(2-aminopropyl ether) (D230)



POSS EP0408



POSS EP0409

Scheme 1. Chemical structure of HBA, D230 and POSSs.

was measured between 25 and 105 °C by increasing the temperature by 5 °C/min. The values were determined in the range 25–40 °C.

3. Results and discussion

^{1}H NMR spectrum of the prepared polysiloxane having glycidoxypropyl groups (PS) is shown in Fig. 1. The ^{1}H peak due to H_a and H_a remains after the reaction, suggesting the presence of 75% of the epoxide ring of GPTMS, which is in good agreement with Ref. [15,16]. The number of epoxy groups attached to PS was estimated as 17.6 under the assumption that PS was composed by hydrolyzed GPTMS.

For epoxy–amine adhesive systems, thermosetting adhesives were obtained by the reaction of primary and secondary amine groups with the epoxide ring [1,17,18], and FT-IR spectra of HBA/D230 and HBA/D230 containing 3 wt% of PS are shown in Fig. 2a and b, respectively. The spectra of binary HBA/D230 samples (Fig. 2a), subjected to different curing times, were used to identify the bands corresponding to the end epoxy groups that belonged to HBA.

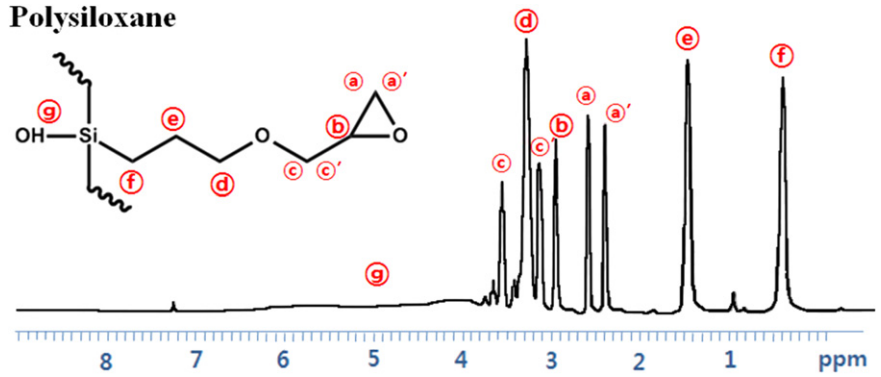


Fig. 1. ^{1}H NMR spectra of PS having glycidoxypropyl groups.

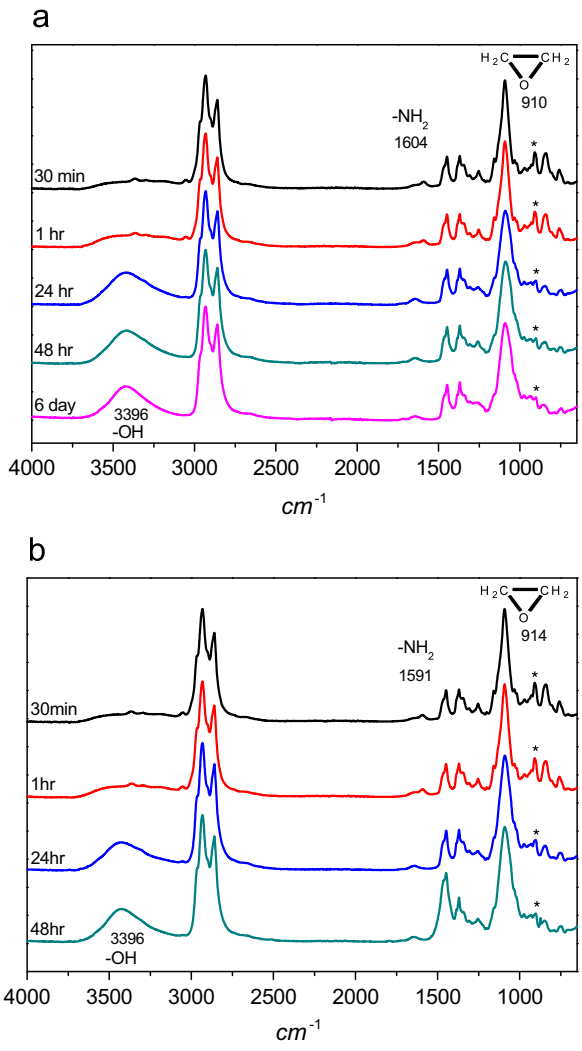


Fig. 2. FT-IR spectra of the adhesives after 0.5, 1, 24 and 48 h. (a) HBA/D230 and (b) HBA/D230 system containing 3 wt% of PS.

For the spectra of HBA/D230 mixture, it was observed that the epoxy ring vibration band, ν_{as} (910 cm^{-1}) [19] decreased during the curing time owing to the opening of the epoxy rings of HBA until it was constant with time. As the curing reaction advanced, the band related to NH_2 at 1604 cm^{-1} decreased while those related to hydroxyl groups, ν_s, 3396 cm^{-1}, increased. This confirmed that the epoxy rings were opened. The band related to NH_2 did not completely disappear after 6 days, implying that some amine groups remained un-reacted during the curing process by amine–epoxy reaction ceasing and/or possibly by homopolymerization of HBA molecules [12].

For the spectra of HBA/POSS mixture, the asymmetric (Si–O–Si) stretching vibration band, ~1075 cm^{-1}, belonging to the strong cage of the POSS, appeared. This band remained unchanged during the reaction because the cages of POSS did not break in the reaction [15]. With the addition of POSS (or PS), the characteristic peaks of the HBA/D230 adhesives containing POSS (or PS) did not change as can be seen in the figure.

The HBA/D230 adhesives, and also the HBA/D230 adhesives containing nanomaterials, were prepared. They were transparent, as shown in Fig. 3, and compared with those of the two commercial adhesives. The addition of POSS (or PS) at this concentration did neither change the curing time nor affect the color.

Generally, in degraded stones, the inside is very dense and the surface very fragile. To optimize the conservation, the adhesives should penetrate the decayed stone deep enough to reach the undeteriorated stone. If this does not happen, an internal weakness will be created, which will eventually lead to further decay like detachments and scaling.

The penetration of an adhesive depends on its viscosity and hence its optimization is crucial in developing new adhesives, particularly those intended for conserving historical monuments. The viscosity of HBA solution was 3020 mPa s and that of the samples of nanomaterial-containing HBA solution prepared for this study was in the range 2500–3500 mPa s.

As the proportion of nanomaterials is a vital parameter for optimizing the formulation of a new adhesive, the viscosity of the adhesive solution was measured 15 min after the addition of D230 to the HBA solution samples containing nanomaterials and the results are plotted in Fig. 4.

As the viscosity of D230 was relatively low, the viscosity of HBA/D230 solution changed to around 360 mPa s. The viscosity observed here may depend on the reactivity between the epoxy group with the amine of D230 and the time that elapses before applying the adhesives. The viscosity of HBA/D230 solution containing 30 wt% of EP0408 is almost twice higher than that containing 10 wt% of EP0408. One interesting phenomenon was that with the addition amount of EP0409 in HBA/D230 system, the viscosity remained unchanged with the amount of EP0409 added within the error range. This proved to be a positive aspect for permeation of the adhesive. Since the nanomaterials were added in the weight base, the mole fraction of the POSS (EP0408 and EP0409) was different, and this may affect the viscosity as well. It was expected that the miscibility, as also the reactivity between the cyclohexyl and glycidyl epoxy group and amine of D230, were different.

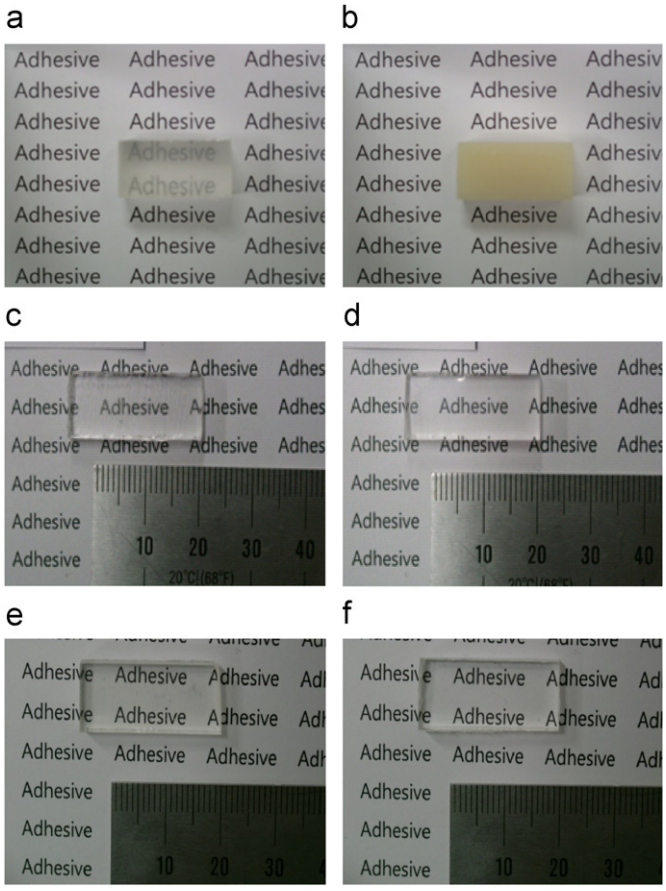


Fig. 3. Adhesives derived from (a) AY103-HY956 and (b) AW106-HV953, (c) HBA/D230; HBA/D230 adhesives containing (d) 7 wt% of PS, (e) 30 wt% of EP0408 and (f) 30 wt% of EP0409.

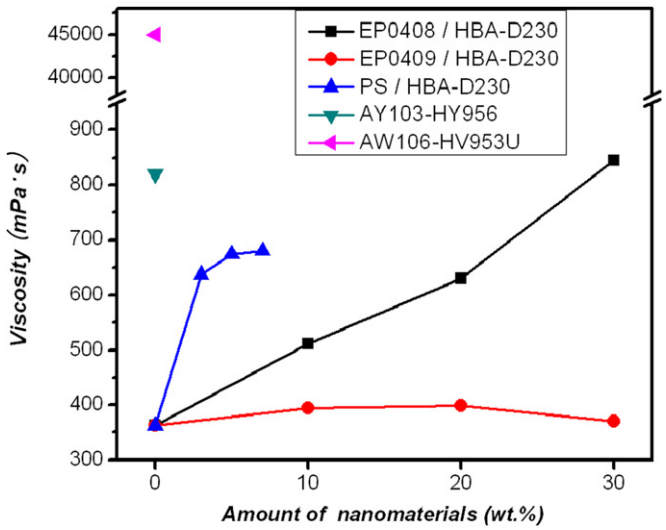


Fig. 4. Viscosity of HBA/D230 containing PS, EP0408 and EP0409.

The viscosity of HBA/D230 solution containing PS increased and reached 680 mPa s for 7 wt% of PS in HBA/D230 solution. For the nanomaterials having the same glycidyl epoxy group (i.e., PS and EP0409), the viscosity of solution having PS was higher than that containing EP0409, which could be due to the higher molecular weight and greater number of glycidyl epoxy groups of PS than those of EP0409.

Because the adhesive properties are closely related to the microstructure of a composite, SEM/EDX measurements were made for deducing information on the morphological properties of the hybrid composites obtained. Representative cross-sectional SEM images of HBA/D230, with and without POSS (or PS), are shown in Fig. 5.

All the samples of the HBA/D230 adhesives containing PS (3, 5 and 7 wt%) show homogeneity, and there is no clear phase segregation. The corresponding EDX image of HBA/D230 adhesives containing 7 wt% of PS confirms that the distribution of Si from PS is homogeneous throughout the cross-section of the HBA/D230 adhesives. The SEM image of HBA/D230 containing EP0409 shows a similar trend until 20 wt% of addition; Si mapping shows that the material is homogeneous, but SEM image shows some clumpy material that may cause microscale immiscibility after the addition of 30 wt% (not shown). In the image of HBA/D230 adhesives containing EP0408, several clumps were observed even with 10 wt% addition and this could prove to be significantly deleterious to the homogeneity of the adhesives at 30 wt% of EP0408.

The tensile strength of the sample was characterized using stainless steel and the results are shown in Fig. 6. The tensile strength increased with the addition of POSS and reached the maximum with the addition of 20 wt%, beyond which it decreased.

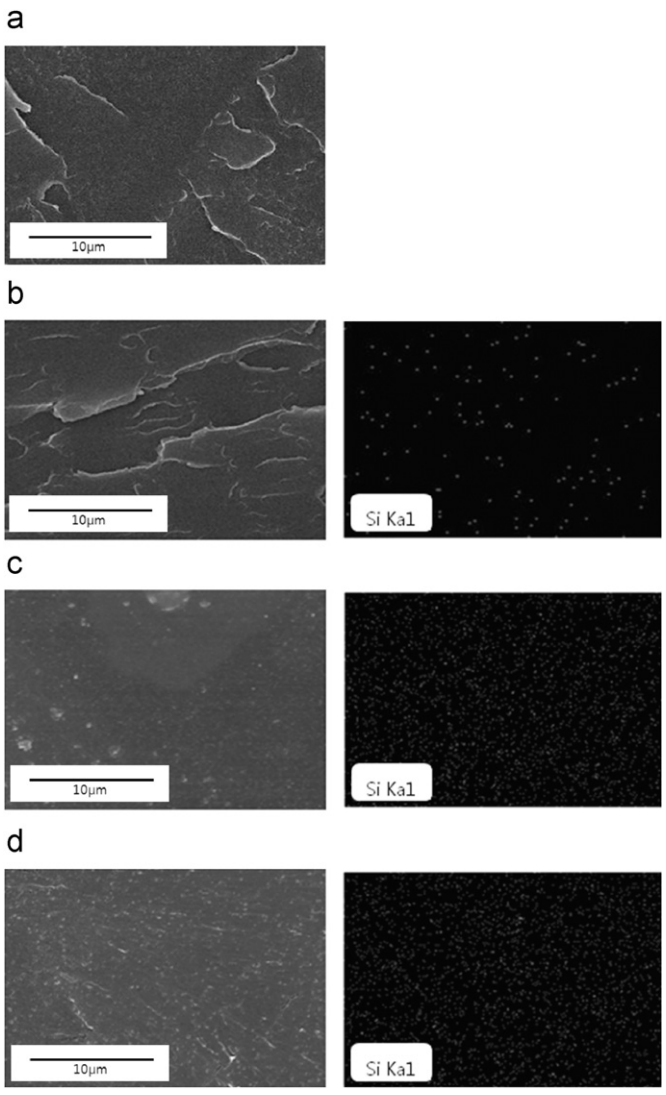


Fig. 5. Cross-sectional SEM and/or EDX (Si) images of (a) HBA/D230; HBA/D230 adhesives containing (b) 7 wt% of PS, (c) 10 wt% of EP0408 and (d) 10 wt% of EP0409.

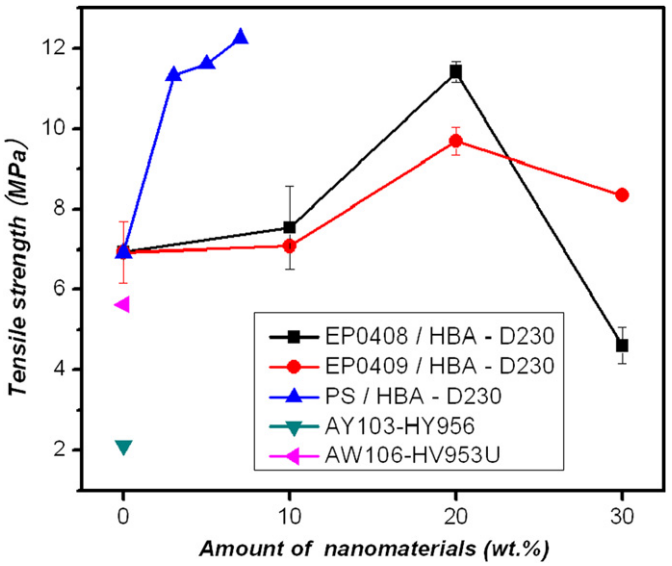


Fig. 6. Tensile strength of HBA/D230 adhesives containing different amounts of nanomaterials.

The tensile strength of the HBA/D230 system also increased with the addition of PS, and the value is consistent with the maximum value of HBA/D230 system containing POSS. It is interesting to see that the addition of bigger nanomaterials having a high number of reactive epoxide groups showed higher value than those having small size and low number of reactive groups such as EP0409. All values are higher than those of commercial adhesives, which may be due to the flexibility of D230 as well as the organic segment of nanomaterials.

Fig. 7 shows the XRD patterns and photomicrographs of fresh granite from Namsan, Korea, which is a widely used stone for Korean cultural heritage monuments. XRD analysis of Namsan granite for the adhesion test in this research shows that the granite consists mainly of orthoclase and quartz and minor amounts of biotite and illite. The bulk porosity is 42.6% and average pore diameter 60 μm, as measured by the porosimeter.

When the granite was treated with the adhesives, its compressive strength in shear values changed with the amount of nanomaterials added to the adhesives, and the results are shown in Fig. 8.

The low compatibility of EP0408 with HBA/D230 system led to the decrease in the compressive strength of HBA/D230 adhesives containing EP0408, but with the addition of EP0409, the compressive strength increased as shown in Fig. 8.

The thermal expansion coefficient was measured and the results are shown in Fig. 9 together with the corresponding values for the commercial AY103-HY956. With the addition of POSS, the values showed different behavior with the functional segment containing epoxy group. With the addition of glycidyl epoxy group (i.e., EP0409), the thermal expansion coefficient increased owing to the aliphatic hydrocarbon segment, while with the addition of nanomaterial having stiff cyclohexyl segment, it decreased. As the thermal expansion coefficient of granite is in the range 2–12 ppm, the coefficient of HBA/D230 adhesives containing EP0408 is comparable to that of the stone materials.

The biggest problem in achieving effective long-term preservation of stone is the application of the adhesive resins to the stone monuments in place. Achieving deep penetration is a problem with most adhesives, especially epoxy resins, which have a poor reputation in this regard. The penetration depth of the adhesives into the granite sample was estimated using a red dye assuming that the adhesives penetrated as deep as the red dye did. The results

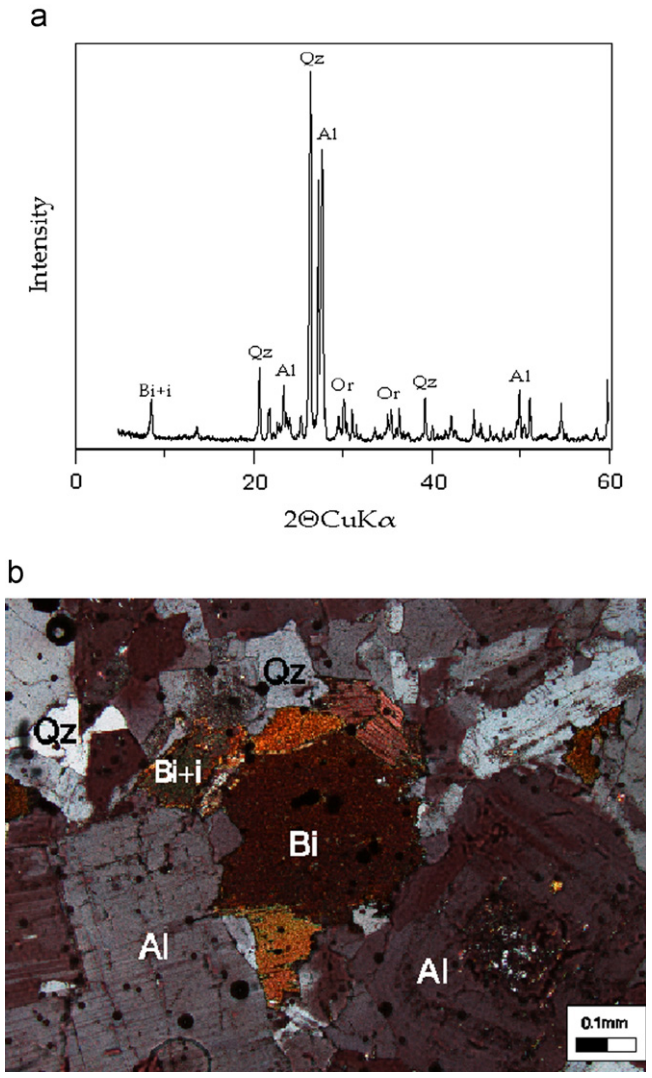


Fig. 7. (a) XRD patterns and (b) microphotographs of Namsan granite (Or=orthoclase, Qz=quartz and Bt=biotite).

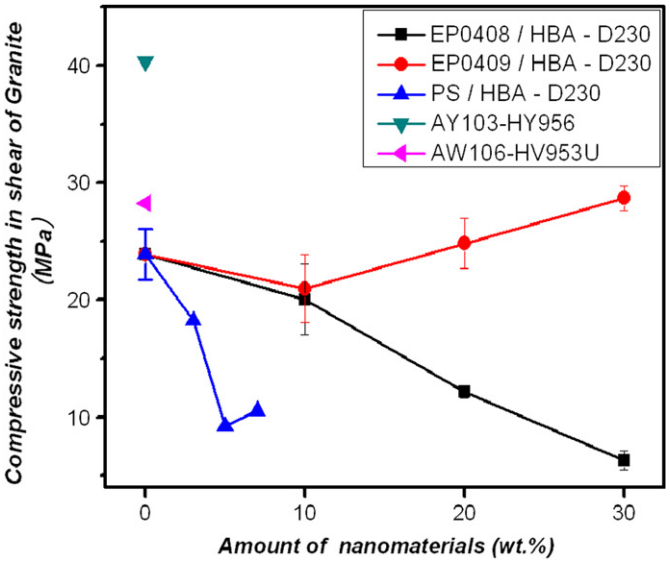


Fig. 8. Compressive strength in shear of granite treated with HBA/D230 adhesives containing different amounts of nanomaterials.

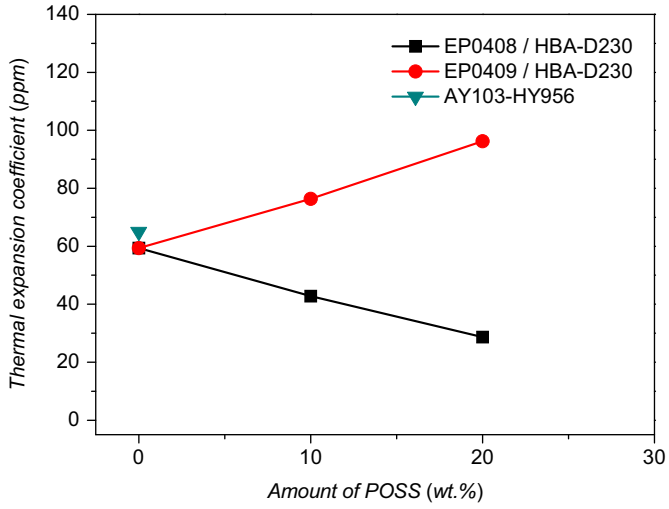


Fig. 9. Thermal expansion coefficient of HBA/D230 adhesives with the addition of EP0408 and EP0409.

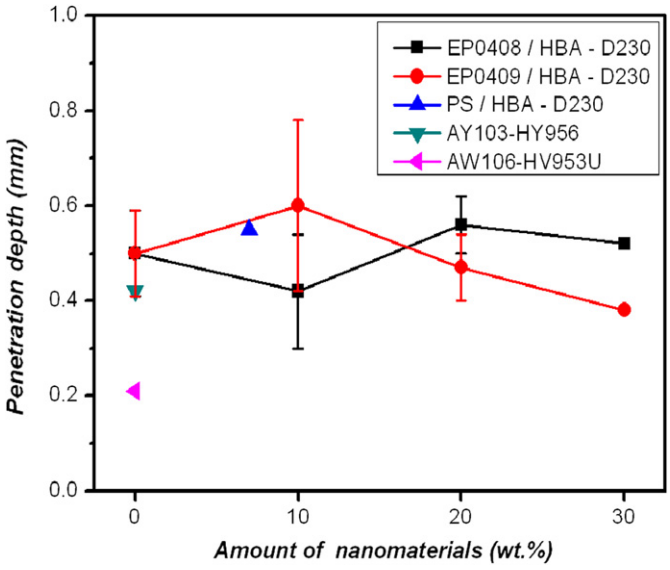


Fig. 10. Estimated penetration depth of nanomaterial-containing HBA/D230 into fresh Namsan granite.

are shown in Fig. 10. The penetration depth was found to be ca. 0.5 mm for all the samples because the viscosities of the solutions developed for this study were of the same order in this viscosity range. The penetration depth is very low, because the granite sample chosen for this study was controlled to be fresh and dense to exclude the effect of the stone sample. The penetration depth of AW106-HV953U adhesives having high viscosity is shallow as compared to that of AY103-HY956 adhesives, implying thereby that there is a dependence of the viscosity.

It must be mentioned here, however, that the low value of the compressive strength in shear and the penetration depth were underestimated, because of the fresh and dense character of the granite sample, which was considered necessary for a reference material.

It is shown that the addition of both POSSs caused an increase in mechanical strength while higher concentrations of the POSS in the HBA/D230 system decrease the strength. In the application of adhesives to the granite, the compressive strength in shear value depends more on the viscosity of the adhesive than on the mechanical strength. The compressive strength in the shear of the adhesive containing PE0409 having lower viscosity is higher than that of the adhesives containing PE0408 having higher viscosity. A similar trend is noticed in the adhesives containing PS. Therefore, optimization of the viscosity of the adhesives is crucial for the formulation of new adhesives in this system.

4. Conclusions

The effects of different functional epoxy groups, and also the proportion of nanomaterials in the color-stable hydrogenated Bisphenol A epoxy resin, were investigated to arrive at the right kind of adhesive for the conservation of stone monuments in open air. The main attributes that render an adhesive suitable for monument conservation are its viscosity, thermal expansion coefficient and compressive strength. The viscosity of HBA/D230 adhesives increased slightly with the addition of nanomaterials. The proportion of the nanomaterial to be added depends on the size and the functional group, which affects the compressive strength in shear when applied to the granite samples. From the relationship between the compressive strength in shear and the viscosity of the adhesives, it is found that optimization of the viscosity is crucial for developing new adhesives for the conservation of stone monuments. Adjustment of thermal expansion coefficient by adding nanomaterials is also important for adhesives to be applied for open-air stone monuments.

Acknowledgment

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