POLYMER-FILLED AQUAMARINE

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The authors have encountered hundreds of polymer-filled aquamarines in the Chinese jewelry market. This treatment can be identified with a standard gemological microscope, since it has characteristics such as a flash effect and relief lines. In addition, some of the filled fractures fluoresce chalky white to long-wave UV radiation. FTIR spectroscopy reveals diagnostic features at ~3100–2850 cm^{-1} that are related to benzene and ethylic C-H bonds in a polymer.

Clarity enhancement of beryl is not new, though by far most attention has been focused on emerald (e.g., Johnson et al., 1999a,b). However, aquamarine has been treated by oiling for some time, and more recently with wax and resin-based fillers such as Opticon (Eliezri, 1998; Johnson et al., 1999a,b). Within the last few years, large quantities of filled aquamarine have entered the Chinese market. Of ~10,000 jewelry pieces tested at the National Gold & Diamond Testing Center of China (NGDTC), we encountered more than 200 items that contained >400 pieces of polymer-filled aquamarine of varying quality. So far, these have been in the form of beads (figure 1), cabochons, and carvings; no filled faceted gems have yet been encountered.

Materials and Methods. For this report, we examined an aquamarine bracelet obtained from a jewelry wholesaler that consisted of 17 reportedly polymer-filled bluish green beads (11.28–12.46 ct; again, see figure 1). The bracelet was disassembled to ensure that there was no interference from the string. In addition, we studied two faceted aquamarines (one oiled and one untreated) for comparison of spectral features.

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At NGDTC, we performed standard gemological testing and Fourier-transform infrared (FTIR) spectroscopy on all the samples. FTIR was conducted with a Nicolet Nexus 470 instrument at room temperature and relative humidity below 40%. Spectra were collected in the range 6000–400 cm^{-1} at a resolution of 8 cm^{-1}, with eight scans per sample at a fixed gain of 1.0. Both transmission and specular reflectance FTIR spectroscopy were performed.

To check whether a lead-based glass such as that used for filling corundum might be present, we performed qualitative chemical analysis of the samples at NGDTC with a Thermo QuantX EC energy-dispersive X-ray fluorescence (EDXRF) spectrometer using parameters optimized for the detection of heavy elements. Operating conditions were 100 second live time, voltage of 20 kV, Rh target, vacuum, and no filter.

Figure 1. These bracelets are typical of the filled aquamarine jewelry currently being encountered in the Chinese market. The beads in the bracelet on the far left (11.28–12.46 ct) were the subject of this study. Photo by Li Jianjun.

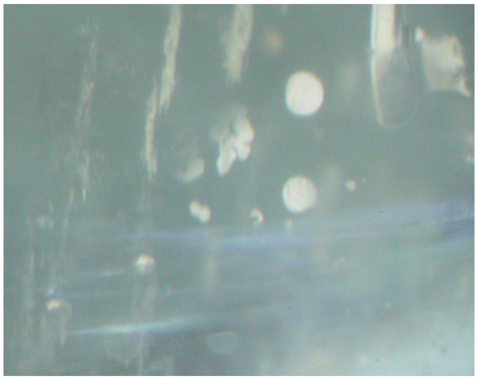
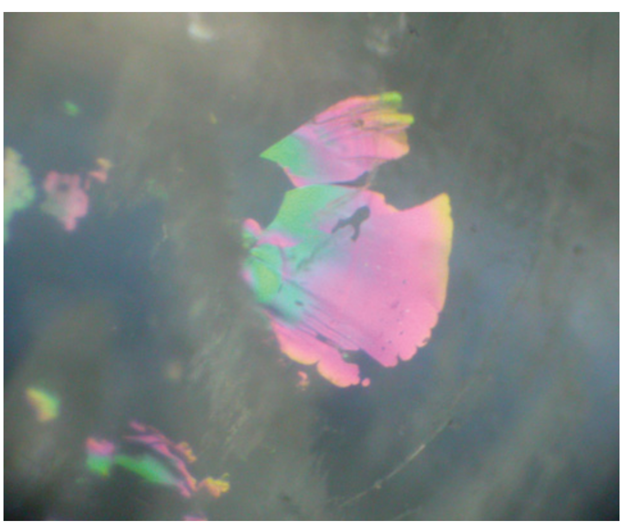


Figure 2. Blue flash effects, high-relief areas, and surface-reaching fissures with cloudy white-appearing regions of reduced transparency were observed in the filled aquamarine beads. Photomicrographs by Li Jianjun; magnified 30× (left) and 15× (right).

Results and Discussion. *Physical and Optical Properties.* The physical and optical properties of the polymer-filled, oiled, and untreated samples are reported in table 1. With the unaided eye, the filled beads exhibited no significant features to arouse suspicion. They were translucent and contained abundant fissures. However, the fractures in a few beads showed a weak, chalky white fluorescence to long-wave UV radiation. This is a good indicator for the presence of a polymer filling (Kammerling and Koivula, 1991). All samples were inert to short-wave UV.

Microscopic Features. With 10× magnification, we observed flash effects in almost every filled bead; some other common microscopic features were high-relief areas (representing incomplete filling) and cloudy areas of reduced transparency that appeared white (figure 2). These are all classic signs of polymer filling (Kammerling et al., 1991; Johnson et al., 1999a; Hainschwang, 2002). Some fractures in the beads showed iridescence (figure 3) as well as a flash effect. When viewing a sample in the direction of the flash, we also observed relief lines where the filling reached the polished surface (figure 4). The underlying fissures did not show a reflective appearance.

Figure 3. This aquamarine bead exhibited iridescence in the unfilled portion of an incompletely filled fracture. Photomicrograph by Li Jianjun; magnified 30×.



Infrared Spectroscopy. FTIR spectroscopy was successful in determining the type of filler material in the beads and in the oiled comparison stone. In spectra taken from the beads (figure 5), the region between 3100 and 2850 cm^{-1} showed features that are diagnostic for polymers. The peaks at 3051 and 3035 cm^{-1} belong to the benzene C-H bond, while those at 2962, 2927, and 2873 cm^{-1} belong to the ethylic C-H bond (Stuart, 2004). The strength of the

TABLE 1. Physical and optical properties of the aquamarine samples studied for this report.

Property	Polymer-filled (17 samples)	Oiled (1 sample)	Untreated (1 sample)
Weight	11.28–12.46 ct	2.27 ct	1.45 ct
Color	Bluish green	Very light blue	Light blue
Pleochroism	Moderate, gray-blue and green-blue	Moderate, blue and greenish blue	Moderate, blue-green and blue
Luster	Vitreous	Vitreous	Vitreous
RI	1.57 (spot reading)	1.575–1.582	1.577–1.583
Birefringence	Not determined	0.007	0.006
SG	2.69–2.73[a]	2.71	2.71
UV fluorescence	Fractures chalky white to long-wave (in a few beads)	Inert	Inert
Microscopic features	Liquid-gas inclusions, fractures and fracture plane reflections, flash effects, iridescent fractures, cloudy areas of reduced transparency, surface relief lines	Liquid-gas inclusion	Three-phase inclusions
Mid-IR absorption features	3051, 3035, 2962, 2927, and 2873 cm^{-1}	2923 and 2858 cm^{-1}	No significant peaks between 3100 and 2850 cm^{-1}

[a] *Seven of the 17 samples were selected randomly for hydrostatic SG measurements.*

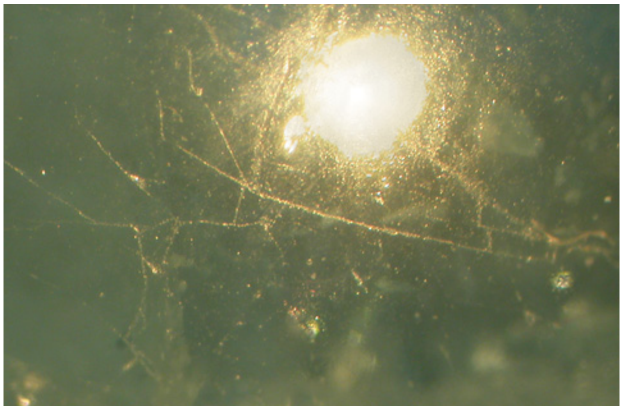


Figure 4. Filled fractures were visible on the surface of the aquamarine beads as relief lines. Photomicrograph by Li Jianjun; magnified 15×.

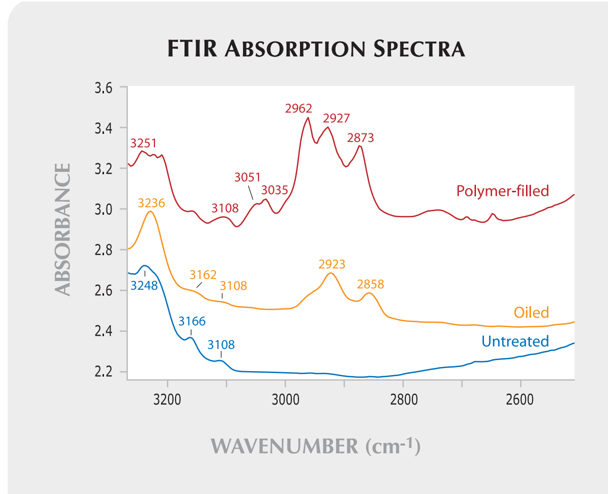


Figure 5. This representative mid-IR spectrum of the polymer-filled beads shows distinct features from polymer impregnation, particularly between 3100 and 2850 cm^{-1}, that are not seen in the oiled and untreated aquamarine comparison samples. The absorption features at 3051 and 3035 cm^{-1} are due to the benzene C-H bond in a polymer. The bands from 3250 to 3100 cm^{-1} are characteristic of beryl. Spectra are offset and shifted vertically for clarity.

filler-related absorption was rather high in some samples, suggesting that some residual substance was present on the surface. We suspect these polymers might be Opticon-like resins or Araldite (Johnson et al., 1999a; Hainschwang, 2002; Lowry, 2006). The differences between these spectra and those of the oiled comparison sample and the untreated stone were apparent (again, see figure 5).

Chemical Analysis. No heavy elements such as lead were detected by EDXRF spectroscopy (Li et al., 2008). Thus, it does not appear that any lead-based glass was used in our samples.

Conclusions. A few of the filled aquamarines in our study revealed abnormal long-wave UV fluorescence, which is a good indicator for polymer filling. Microscopic evidence of polymer filling also included surface relief lines with no corresponding reflective internal features, as well as flash effects when the samples were viewed nearly parallel to filled fractures.

In our experience, about 15% of the aquamarines with poor clarity (i.e., mostly beads, cabochons, and carvings) currently in the Chinese market have been filled. Although we have not yet encountered polymer-filled faceted samples in the marketplace, this treatment could easily be used on included faceted gems.

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