Cambridge Polymer Group

Cracking in Polycarbonate Syringes

By Dr. Stephen Spiegelberg, Chief Scientific Officer

Summary

The appearance of cracks in a device is the start of many root cause analysis projects. Because cracks may affect the performance or safety of the device, or at a minimum, the appearance of the device, determining the reasons for the cracking is critical. This type of root cause analysis frequently requires a deep knowledge of material science and a series of tests and judicious conditioning to try to mimic the cracking behavior. Once the conditions are known, solutions to prevent cracking can then be investigated. This application note describes the root cause investigation of cracks that appeared in polycarbonate syringes that had been accelerated aged as part of a shelf-storage study. The results of the study were unexpected and pointed out a few issues with the manufacturing line.

Client Request

A client had been producing polycarbonate syringes in a three-shift operation. As part of an internal study to extend the shelf-life of the syringes, they were conducting an accelerated aging study whereby the syringes were held at 55 ºC for a period of time. A percentage of the syringes subjected to this accelerated aging began to show haziness and microcrack formation (see Figure 1). The client requested assistance in determining the reasons for the cracking so they could avoid this issue in real time aged samples.

Figure 1: Microcracks forming in PC syringe.

Root Cause Investigation

As part of the root cause investigation, CPG gathered information about the design and manufacturing process for the syringes. The syringes had a secondary component attached to the luer lock of the syringe, held in place with a UV-curable epoxy. In addition to the polycarbonate, the plunger was comprised of acrylonitrile-butadiene-styrene. The syringes were ethylene oxide sterilized, and aging was conducted in a warm, humid environment. The client reported never observing cracking in unaged samples.

Following this information gathering step, the client provided examples of aged samples that showed cracking, as well as unaged samples with no cracking. Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS)

conducted on the samples showed a raised pattern on the polycarbonate that had only the presence of carbon and oxygen (see Figure 2). FTIR analysis of scraped portions of the hazy area confirmed that the hazy area contains carbon and oxygen in the form of hydroxyls (see Figure 3).

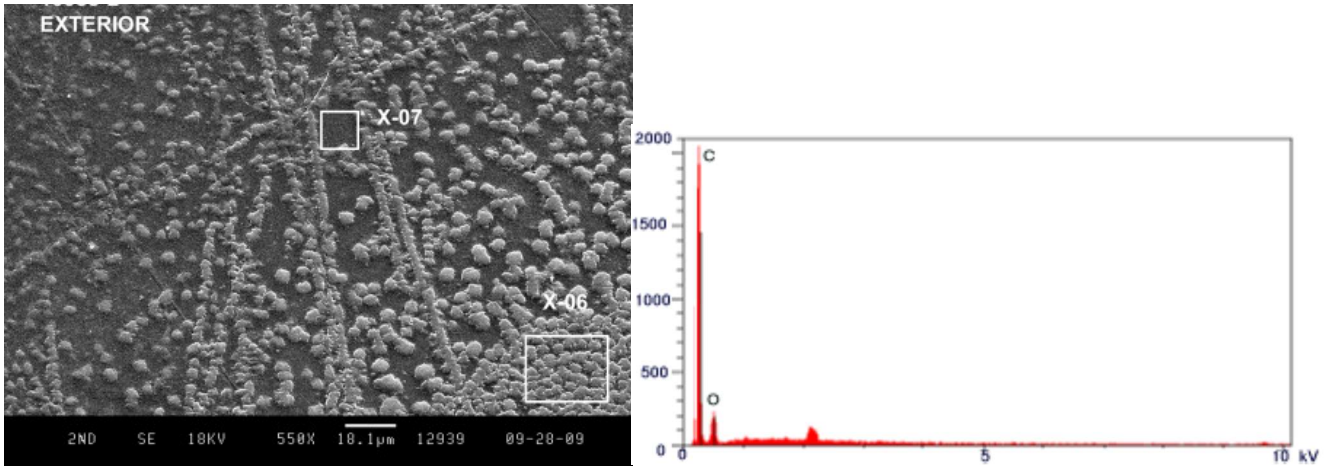

Figure 2: SEM of hazy area at 560X (left), and EDS spectrum of region in X-06 (right).

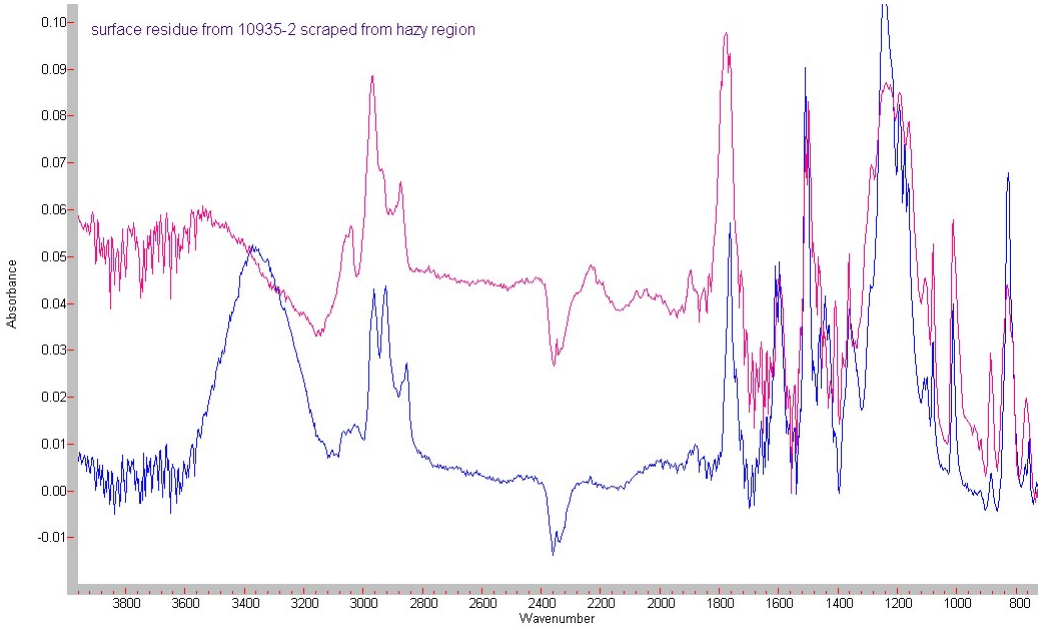

Figure 3: FTIR spectrum of hazy area (blue) vs. clear area (red). The red spectrum is consistent with polycarbonate. The blue arrow indicates the region in the blue spectrum corresponding to hydroxyl groups.

To determine if one of the components was off-gassing a volatile component that could be causing the haziness or cracking, thermal gravimetric analysis (TGA) was performed on the individual components (Polycarbonate barrel, ABS plunger, and UV-cured epoxy) after immediate manufacture (t=0 months) and after shelf storage for 13 months (Figure 4). The results demonstrated little to no volatiles present in the polycarbonate and ABS, even up to 250 °C, and no notable differences between the aged and unaged samples. The UV-cured epoxy, however, did show more notable mass loss, with the unaged sample showing notably more mass loss than the aged sample, suggesting that some volatiles may be present, likely due to uncured epoxy (see Figure 4), and that these are either driven off, or forced to cure further in the aged sample.

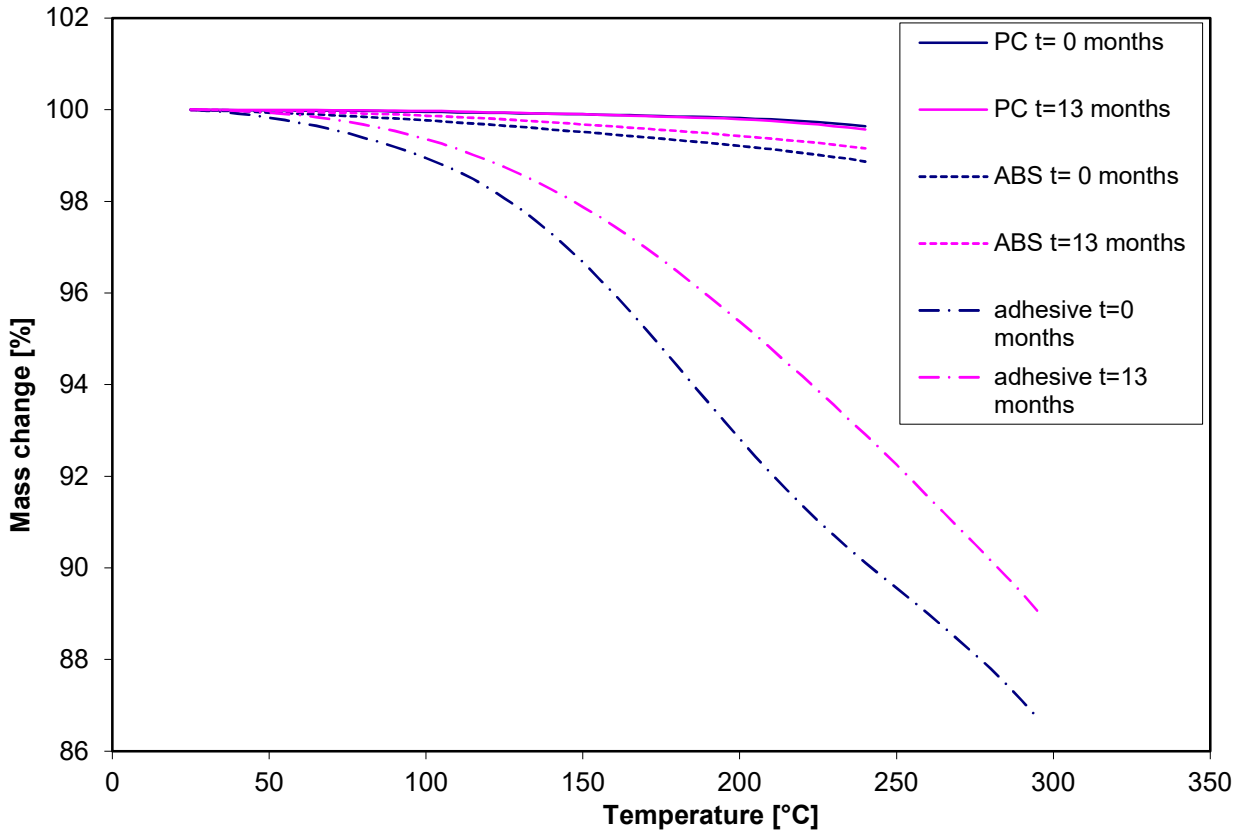

Figure 4: Thermogravimetric response of aged and unaged polycarbonate barrel, ABS plunger, and cured adhesive. The newly cured adhesive showed the largest mass loss.

In a continued investigation of client-provided syringes, one of our scientists performing scanning electron microscopy noticed patterns in the hazy region in the form of curved lines that were not consistent with their experience of usual crack mechanisms. Reducing the SEM magnification demonstrated that the observed patterns were consistent with fingerprints (Figure 5). As fingerprints contain fatty acids[1] which are hydrocarbons that contain oxygens and may contain hydroxyl groups, the hydroxyls identified in the FTIR and supported by the EDS were suspected to be from skin oils. An investigation by the client on the manufacturing site found that some product assembly staff were not wearing gloves. They also found that some assemblers were wiping down the syringes with isopropyl alcohol, a step which was not included in the manufacturing protocol.

With this additional information, a study was conducted with newly prepared syringes, using the following variables to see if haziness or cracking resulted after aging at 55 °C for 5 weeks:

1. Model hand oil (palmitic acid, steric acid, oleic acid, cholesterol) (yes, no)
2. IPA wipes (yes, no)
3. Unreacted epoxy monomer (yes, no)
4. ABS plunger present (yes, no)
5. Relative humidity (high, low)
6. ETO sterilization (yes, no)

[1] Kim, Y., Choi, Ws., Choi, E.J. et al. Evaluation of fatty acids in groomed fingerprint by gas chromatographic analysis using various extraction solvents and treatment methods. J Anal Sci Technol 10, 29 (2019). https://doi.org/10.1186/s40543-019-0188-y

A design of experiment (DoE) study was conducted with these variables, with visual assessment for the formation of haziness and cracking. The results are summarized in Table 1. In general, haziness resulted if unreacted monomer or hand oil was present along with the heat of aging, although hand oil only caused haziness if coupled with humidity and sterilization. Cracking occurred in the presence of unreacted monomer, and also when sterilization was coupled with high humidity. Interestingly, if an IPA wipe was included, even with unreacted monomer or hand oil, haziness and cracking did not occur, indicating that this step was effective in reducing the influence of these contaminants.

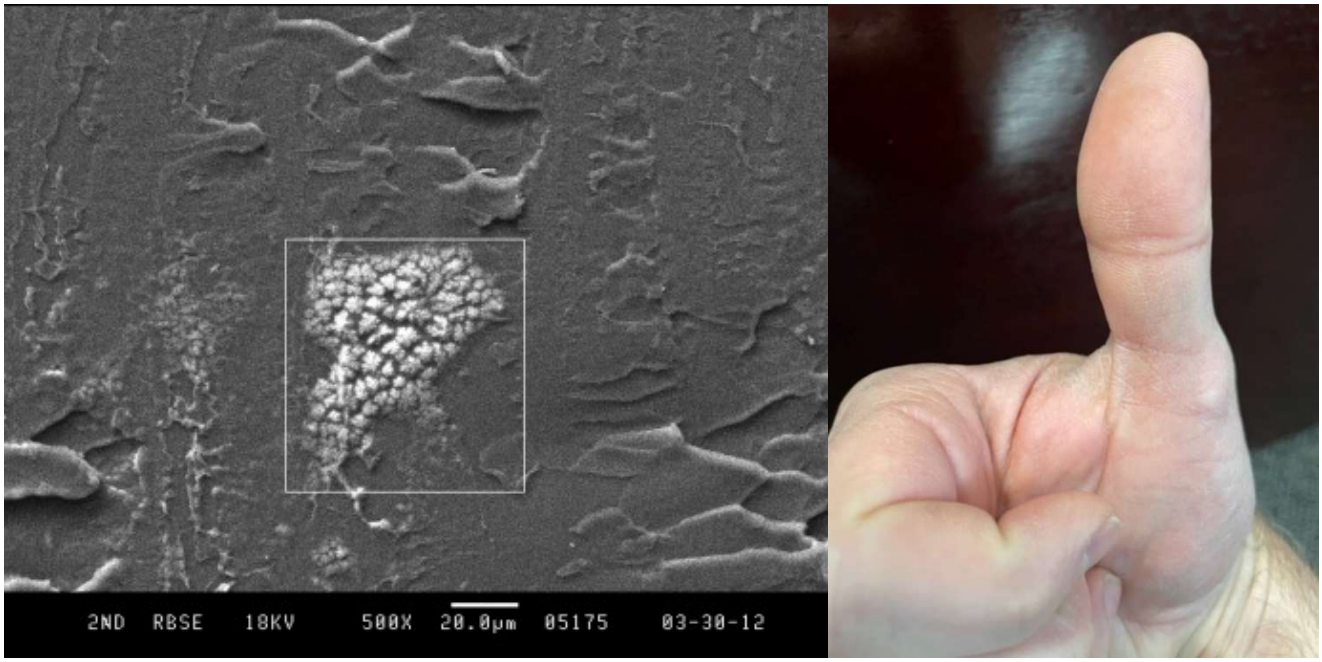

Figure 5: Feature in scanning electron microscopy found in a hazy region. Other features show patterns consistent with fingerprints. The EDS signal of this location showed sodium, potassium, and chlorine, all ions associated with skin salts.

Table 1: Test conditions that led to haziness or cracking.

Condition	Haziness?	Cracking?
IPA wiped samples	No	No
Plunger Presence	No	No
Unreacted epoxy monomer	Yes	Yes
ETO sterilization	No	Yes (if included with hand oil)
Humidity	No	Yes (*if included with ETO)
Hand oil	Yes (if included with humidity, ETO)	No

Conclusions

This case study demonstrates the importance of a structured strategy for problem solving, leveraging material science in the aid of determining root-cause. In addition, it demonstrates the value of experience in looking for anomalies in experimental data. The results from this study showed that one single variable was not responsible for the haziness and cacking of the polycarbonate samples. Rather, it was a combination of contaminants and test conditions that resulted in haziness and cracking. Because of this investigation, the client identified some deviations in their manufacturing process, one of which led to the identification of more product failures, and one of which reduced product failures. The latter (IPA

wipe) was further investigated to ensure that it did not have any undesirable effects and was eventually written into the cleaning procedure. The client also increased the cure time for the UV-curable epoxy to reduce the amount of epoxy monomer and ensured that assemblers were all wearing gloves.

About Dr. Stephen Spiegelberg

Dr. Stephen Spiegelberg is the co-founder of Cambridge Polymer Group. With a career spanning over 25 years, Dr. Spiegelberg has consistently demonstrated an unwavering commitment to ensuring the safety and compatibility of medical devices and materials. At Cambridge Polymer Group, he directs a team of scientists performing contract research, analytical testing, failure analysis, and product development for the biomedical community and other fields. In 2022, ASTM International presented Spiegelberg with the Award of Merit, their highest recognition for distinguished service, for his contributions to the ASTM F04 Committee on Medical and Surgical Materials and Devices. He received his BS in Chemical Engineering from UW-Madison, and his Ph.D. in Chemical Engineering from the Massachusetts Institute of Technology.

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