Characterization of Highly-Crosslinked Acrylate Polymers

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Highly-Crosslinked Polyacrylate

My main project this semester was to begin work on an industry project funded by Boehringer Ingelheim Vetmedica, an animal pharmaceutical company. Some of the products they make are vaccines which utilize a certain type of polymer which not only thickens the vaccine, but also acts as a time-release agent due to the active compound being entangled in the polymer structure. The type of polymer they asked us to study is called Carbopol. There are several different types of Carbopol polymers but all are polymers of acrylic acid crosslinked with polyalkenyl ethers or divinyl glycol, in this case it is crosslinked with pentaerythritol allyl ether. These polymers readily absorb water, become hydrated, and swell.

![Figure 1](image1.png)

*Figure 1:* a) General structure of poly-acrylic acid b) Structure of the pentaerythritol allyl ether crosslinking agent

Our task was to investigate the loss of thickening ability in the polymer after their sterilization procedures through the use of powerful and sensitive techniques such as NMR, IR, and thermal analyses. However, the major hurdle we are still grappling with is solubility issues due to the highly-crosslinked nature of the compound.

![Figure 2](image2.png)

*Figure 2:* General structure of Carbopol polymers
Photoacoustic IR Spectroscopy

Due to problems with the solubility of Carbopol, techniques which required little to no sample preparation were investigated as primary methods of characterization. The first of these is the technique of FT-IR Photoacoustic Spectroscopy which has been pioneered by John McClelland of The Ames Laboratory\(^1\).

Infrared Spectroscopy is a powerful, non-destructive, analytical technique for investigating the vibrational properties of molecules. It exploits the fact that molecules absorb specific frequencies of infrared radiation that are characteristic of their structure and which excite them to a higher vibrational energy level. It is used to determine the types of chemical bonding that are present in a sample. Photoacoustic Spectroscopy (PAS) is unique because it does not require that the sample transmit the IR radiation. Instead, it directly measures IR absorption by sensing absorption-induced heating of the sample which creates a thermal pressurization of the surrounding gas. This basically amounts to a sound wave at the sample surface which can be detected by a microphone.

![Photoacoustic IR Spectroscopy](image)

**Figure 3:** FTIR-PAS absorbance spectra of two Carbopol samples (black and red) and uncrosslinked polyacrylic acid (blue)

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>517-524</td>
<td></td>
</tr>
<tr>
<td>648</td>
<td></td>
</tr>
<tr>
<td>806</td>
<td>CH(_2) (rocking)</td>
</tr>
<tr>
<td>~875</td>
<td></td>
</tr>
<tr>
<td>1049-1053</td>
<td></td>
</tr>
<tr>
<td>1115</td>
<td>C-O-C (stretching)</td>
</tr>
<tr>
<td>1173</td>
<td>Related to 1250</td>
</tr>
<tr>
<td>1250</td>
<td>C=O(st) or O-H(bend)</td>
</tr>
<tr>
<td>1420</td>
<td></td>
</tr>
<tr>
<td>1454</td>
<td>CH(_2) (bending, out of plane)</td>
</tr>
<tr>
<td>1717</td>
<td>C=O (stretching)</td>
</tr>
</tbody>
</table>

**Table 1:** Peak assignments of FTIR-PAS absorbance spectra\(^2,3\)
Thermal Analysis of Carbopol

Thermal analysis is a strong tool for characterizing polymers. Both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been used to investigate our polymer samples. TGA is a very simple technique which involves heating a sample at a defined rate and recording the mass lost as the sample decomposes. This can give information about the composition of the sample as well as its thermal stability. In this case, it was used to determine if our samples contained a large amount of water, especially given the very hygroscopic nature of Carbopol. According to the data shown in figure 4, there does not appear to be an especially large amount of water present in the samples. In order to investigate this further, a more powerful technique called TGA-MS could be used which sends the evaporated sample gases to a mass spectrometer to determine their chemical composition.

![Figure 4: TGA traces of two Carbopol samples (black and red) and uncrosslinked polyacrylic acid (blue)]](image)

DSC was also used to investigate the thermal characteristics of Carbopol. This technique measures the change in the amount of heat required to increase the temperature of a sample measured as a function of temperature. The basic principle of this method is that when a sample undergoes phase transitions, such as the glass transition of polymers, more or less heat will need to flow into the sample to continue to raise its temperature. It has been shown that the degree of crosslinking in acrylate-based polymers has an effect on the glass transition temperature ($T_g$). Thus, this technique can be used to determine if the amount of crosslinking has any effect on the loss of thickening power observed after sterilization of the vaccines containing Carbopol.
**Figure 5:** Representative DSC trace of Carbopol showing a $T_g$ at approximately 105°C

**Figure 6:** Representative trace of uncrosslinked polyacrylic acid showing no discernable $T_g$

**Nuclear Magnetic Resonance**

Nuclear Magnetic Resonance (NMR) is an incredibly powerful tool for chemical analysis which can give a large amount of information as to the chemical environments of both the hydrogen atoms and carbon atoms in our sample. This is most often done on
solutions of the sample and given the solubility issues of Carbopol, investigations are still underway as to the best solvent system for this case.

**Conclusion**

We have been investigating a variety of methods for the characterization of allyl pentaerythritol-crosslinked polyacrylic acid, also known as Carbopol. This polymer is often used in animal vaccines for its thickening properties and its ability to act as a time-release agent in the release of the active vaccine agent. A problem has arisen in which the polymer loses its thickening properties upon sterilization of the vaccine. We strongly suspect that there is a link between the chemical structure of the polymer, specifically the amount of poly-oxygenated crosslinks, and its physical properties. We have been investigating the use of FTIR-Photoacoustic Spectroscopy (PAS), thermal analyses such as TGA and DSC, and NMR to provide a set of tools with which to test our hypothesis.
References

