# Differentiation by FT-IR of Absorbable Polyesters Used in Production of Surgical Meshes

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**Statement of Purpose:** The production of absorbable surgical meshes in the medical device industry depends upon reliable analytical data for the accurate characterization of the multiple polymeric components used in the production of medical devices. Distinguishing between polymers such as poly(L-lactide), poly(glycolide), and copolymers thereof, is critical to ensuring high levels of quality for meshes that depend upon specific degradation and strength retention profiles provided by the specific polymeric components. However, distinguishing aliphatic polyesters can be difficult due to similarities in chemical structure. This requires analytical techniques that are sensitive to these subtle differences. Poly-Med, Inc. has used FT-IR to characterize and differentiate three custom polymers of poly(L-lactide-co-TMC), poly(glycolide-co-TMC), and poly(*para*-dioxanone) (referred to herein as PL, PG, and PD, respectively) that are used in the production of surgical meshes. PL, PG, PD contain greater than 85% by mole of L-lactide, glycolide, and *para*-dioxanone repeat units, respectively. We hypothesize that FT-IR analysis can be used to successfully distinguish these aliphatic polyesters according to differences that are manifested in their FT-IR absorption spectra.

**Methods:** Polymers were synthesized by ring-opening polymerization by methods similar to that described in US Patent No. 6,342,065[1]. FT-IR was performed using a salt plate method on a Spectrum One FT-IR spectrometer. The polymer was dissolved in chloroform at 8 mg/ml, and the solution was pipetted onto a clean salt plate surface and allowed to dry for at least 30 minutes prior to analysis.

**Results:** FT-IR analysis of PL, PG and PD yielded similar absorption spectra with subtle differences in the 1770-1000 cm$^{-1}$ region, as seem in Figure 1. Frequencies of major absorption bands are listed in Table 1 for each polymer and are compared to literature values for PLLA[3]. Since these materials are all based upon an aliphatic, polyester structure, the main functional groups associated with these polymers are ester bonds, methylene, methyl, and ether groups. Each material displays a strong absorption corresponding to the C=O stretch in the 1765-1735 cm$^{-1}$ region; however, PD shows a doublet at 1748 and 1736 cm$^{-1}$, which is significantly lower frequency than what is observed for PL and PG. Other notable absorption bands for the specific polymers are as follows: PL displays bands at 1455 (asymmetric CH$_3$ bending[2,3]), 1383 (symmetric CH$_3$ bending[2]), 1361, 1184 (asym. C-C(=O)-O stretch[2]) and 756 cm$^{-1}$. PG displays bands at 1424 and 1398 (both attributed to CH$_2$ scissoring[2]), 1287, 1157, and 1090 cm$^{-1}$. PD has bands at 1456 and 1431 (CH$_2$ scissoring[2]), 1207 (asym. C-C(=O)-O stretch[2]), 1136 (sym. C-O-C stretch, ether[2]), and 724 cm$^{-1}$ (CH$_2$ rocking[2]). It should be noted that PG and PD display CH$_2$ scissoring bands near 1455 cm$^{-1}$, which is shifted to a lower frequency than typically observed (1465 cm$^{-1}$) due to the close proximity of CH$_2$ groups and ester bonds[2].
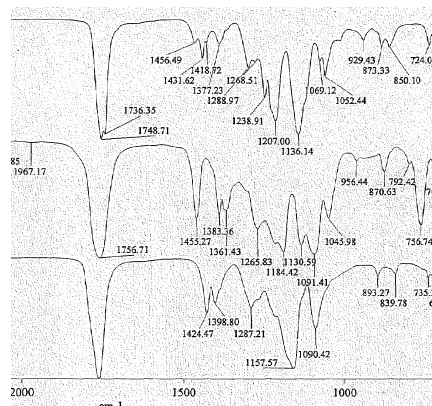


Figure 1. FT-IR spectra of PDO, poly(L-lactide-co-TMC), and poly(glycolide-co-TMC), from top to bottom.

Table 1. FT-IR analysis of PLLA, PGA and PDO.

| PG | PD | PL | PLLA[3] | Description[2,3] | Assignment[2,3] |
|---|---|---|---|---|---|
| 1761 | 1736 1748 | 1757 | * | C=O stretch | $\nu$C=O |
| 1424 1398 | 1456 1431 | 1455 | 1458 | Asymmetric bending | $\delta_{as}$CH$_3$ (PLLA) $\delta_{as}$CH$_2$ (PDO, PGA) |
| -- | -- | 1383 | 1386 | Symmetric bending | $\delta_s$CH$_3$ |
| -- | -- | 1361 | 1368 1360 | C-H bend + symmetric CH$_3$ bend | $\delta_1$CH + $\delta_s$CH$_3$ |
| 1287 | 1207 | 1184 | 1215 1194 1184 | Asymmetric C-O-C stretch + asymmetric CH$_3$ rocking | $\nu_{as}$COC + r$_{as}$CH$_3$ |
| 1157 1090 | 1136 1069 | 1130 1091 | 1107 1089 | Symmetric C-O-C stretch | $\nu_s$COC |
| | 724 | 756 | -- | CH$_2$ rocking | rCH$_2$ |

* values were not reported

**Conclusions:** The major differences in chemical structure between these three polymers are the methyl group in PL, methylene groups in PG and PD, and ether groups in PD. These differences result in the presence, absence, or shifting of particular bands in the absorption spectra. For instance, PLLA lacks the bands associated with methylene scissoring and symmetric ether stretching. PG lacks asymmetric and symmetric methyl bending, as well as symmetric ether stretching. And PD displays absorption bands for methylene bending and ether stretching vibrations, but it lacks bands for asymmetric and symmetric methyl vibrations. It should also be noted that the C=O stretching vibration for PD is shifted to a lower frequency than that of either PL or PG, thereby distinguishing PD from PL and PG. This shift could be explained by the close proximity of ester groups in PLLA and PGA, where opposing dipoles could increase force constants and shift the absorption bands to higher frequencies. According to these cumulative results, the specific FT-IR absorption bands corresponding to C=O, -CH$_3$, -CH$_2$-, and C-O-C can be utilized to distinguish PL, PG, and PD, despite only subtle differences in chemical structure.

**References:**
1. Shalaby, S.W. et al, US Patent No. 6,342,065 (2002).
2. Silverstein R.M. *Spectrometric Identification of Organic Compounds,* 7$^{th}$ Ed, John Wiley & Sons, 2005.
3. Zhang J. Macromol. 2004;37:6433-6439.