

Thermoplastic Polycarbonate-urethane with Covalently-Bonded C-18 End Groups: Surface and Bulk Properties

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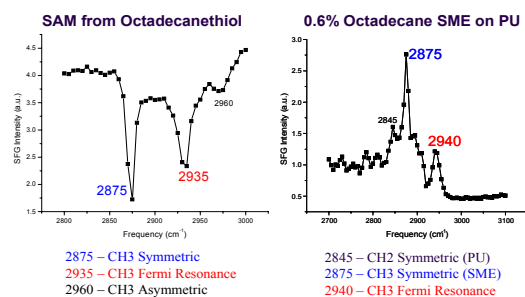
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Statement of Purpose: An unusual combination of toughness and biostability make aromatic polycarbonate urethanes (TPCU) useful in long-term implants, including prosthetic joints, spinal fixation devices and neural stimulation leads. Since the introduction, of Bionate[®] TPCU (formerly Corethane[™]) this family of thermoplastic biomaterials has been made by *batch* synthesis without catalysts, additives, or processing aids. This, and its high MW contribute to occasional processing difficulties in extrusion and injection molding relative to other TPUs, e.g., Tecoflex and Pellethane polyetherurethanes, which both contain N, N'-ethylene bis-stearamide, a.k.a. "Advawax[®]". This reaction product of stearic acid and ethylene diamine has a MW of 593 D and melts at 138°C. It is highly surface active but also internally lubricates the TPU chains in the melt at ca. 200 ± 25°C. Used at a bulk concentration of 0.25 to 5 wt%, Advawax[®] also reduces polymer self-adhesion and improves mold release. Although stearyl groups in polymer surfaces have often been associated with favorable blood-materials interactions^{1,2}, the low MW of Advawax allows it to leach from polymer surfaces, an undesirable property in chronic implants. Here we show that covalently-bonded C18 end groups on a TPCU can simultaneously provide permanent C18 surface modification, molecular weight control, and improved processability, while preserving polymer toughness.

Methods: Polymers were bulk synthesized from MDI, BD and polycarbonate-diol on a *continuous* twin-screw extruder/reactor by including octadecanol as a chain stopper. This monofunctional alcohol, CH₃(CH₂)₁₇OH, is appended to the linear polymer by a urethane linkage and can occupy only terminal positions on the backbone. Film was solution-cast on a web coater with HEPA filtered ovens. Its surface was characterized in air by Sum Frequency Vibrational Spectroscopy (SFG) and compared to a SAM surface of octadecanethiol on gold. MW was determined by PS-calibrated GPC with DMF/LiBr solvent on Stryragel HT 3, 4 & 5 columns. Melt flow rate was determined at 224 °C and 2160 g load (ASTM D-1238). Tensile properties measured according to ASTM D-1708.

Results/Discussion: Advawax has been a (sometimes unknown) determinant of performance of common thermoplastic polyurethanes for as long as they have been used as biomaterials, contributing to blood-material interactions and environmental stress cracking response. A less-fugitive alternative to this additive is needed. The figure shows SFG spectra for (a) octadecanethiol SAM, and (b) for Bionate[®]-55D TPCU with octadecane/C18 end groups. The methyl symmetric and Fermi resonance peaks of octadecane are observed at 2875 and 2935 cm⁻¹, respectively. Negative peaks in the SAM spectrum are caused by destructive interference of the resonant methyl and non-resonant gold signals. Although the *bulk* octadecane end group concentration in the TPCU is only 0.6 wt%, methyl peaks dominate the Bionate SFG spectrum, with only an additional small peak at 2845 cm⁻¹ assigned to methylene groups, most

likely from adjacent alkyl chains on the end group. In each plot the ordinate is SFG Intensity [a.u.] and the abscissa is Frequency [cm⁻¹].



Wt. % SME	Mw	MFR (g/10min)	UTS (psi)	UE (%)
0.2	295000	18.3	8988	372
0.6	279000	40.7	8990	404
1.0	109000	Too high	4924	455

TPCU molecular weight decreases, and melt flow rate increases with increasing end group concentration indicating improved processability (Table). Tensile properties are unchanged at a bulk concentration that produces the significant surface modification measured by SFG. This MW data and results from *admixed* Advawax (not shown) suggest that improved processability is related to both reduced MW and to the plasticizing effect of the C-18 end groups.

Conclusions: A composition change of 0.6 wt% has produced a dramatic surface change in this TPCU while significantly reducing melt viscosity. SFG, a highly surface-specific and sensitive characterization method,⁴ confirms a surface concentration of methyl groups, comparable to an octadecanethiol SAM, even though methyl groups are absent in the TPCU backbone. At an end group concentration sufficient to give the desired surface modification and processing improvement the excellent tensile properties of the unmodified base polymer are retained. Better lot-to-lot consistency from continuous synthesis has previously been demonstrated³, and is an additional improvement over batch-synthesized TPUs in device applications. Future studies will compare biostability of the C-18 TPCU to controls. (Other hydrophobic end groups have been shown to *enhance* in vivo biostability of thermoplastic polyurethanes.⁵)

References:

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