INTRODUCTION: A series of segmented polyurethanes with surface modifying endgroups (SMEs) were synthesized and blended with phenoxy resin to precisely control the surface chemistry of the resultant polymer. The surfaces of these polymer blends were then characterized using sum frequency generation (SFG) vibrational spectroscopy and contact angle goniometry. The precise surface chemistry of these polymers will allow, for the first time, high-strength, structural biomaterials to be used for molecular in vitro experiments including: protein adsorption, cell adhesion, and complement activation studies. Previously, systematic in vitro experiments designed to investigate the effect of surface chemistry have been performed on substrates with self-assembled monolayers. Although these studies have provided valuable insight into the effect of surface chemistry in vitro on model systems, it would be beneficial to perform parallel studies on 'real' biomaterials that could be used for devices and prosthetic implants. Before such studies are performed, it is essential to carefully characterize the surface so proper correlations between surface chemistry and in vitro response can be made. For this purpose, we employ the use of SFG, which is an extremely sensitive surface specific vibrational spectroscopy. A major limitation of several analytical methods used to characterize biomaterial surfaces is the lack of molecular identity with complete surface specificity. SFG is a relatively new nonlinear optical technique that provides molecular level information at only surfaces or interfaces. Not only is the technique surface specific, but it is also sub-monolayer sensitive.

MATERIALS & METHODS: Recently, SFG has been applied to biomaterial surfaces with great success. SFG is a laser technique based on second-order nonlinear optics that, under the electric dipole approximation, is forbidden in amorphous, isotropic, or centrosymmetric media. At surfaces or interfaces, centrosymmetry is broken and SFG is then allowed. Although polymers are amorphous, polar ordering of functional groups occurs at surfaces or interfaces and thus, become SFG active. The series of SME polymers used for this study were BioSpan®-S (between 0 and 0.1000 wt% bulk PDMS) and BioSpan®-F (between 0 and 0.0500 wt% bulk perfluorinated hydrocarbon).

DISCUSSION: Figure 1 shows the SFG spectra for a series of BioSpan®-S and phenoxy blends. Phenoxy has a signature peak at 2865 cm⁻¹ while the PDMS in BioSpan®-S has a signature frequency at 2905 cm⁻¹. At a bulk PDMS concentration of only 0.0200 wt%, a large peak at 2905 is already apparent, although by careful peak fitting, a small contribution of PDMS can be detected at a concentration of as little 0.0001 wt%. Figure 2 shows the SFG spectra for a series of BioSpan®-F and phenoxy blends. The signature peak for BioSpan®-F is observed at 2850 cm⁻¹ and is apparent at bulk F concentrations of 0.01 wt%

CONCLUSION: These results demonstrate the surface specificity of the SFG technique and the ability of producing polymers with precise surface chemistry. Also, the results clearly show the surfaces are dominated by the SMEs even at small bulk concentrations. With these polymers well characterized, protein adsorption experiments are now being performed to determine the affect of surface chemistry.

![Figure 1: SFG spectra of a series of BioSpan®-S/phenoxy blends between 0 and 0.1000 wt% PDMS bulk concentration.](image1)

![Figure 2: SFG spectra of a series of BioSpan®-F/phenoxy blends between 0 and 0.05 wt% F.](image2)

This work was supported by NIH-SBIR Grant No. R43 HL57087.