Smart Biodegradable POSS-Polycaprolactone PolyUrethanes

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Simuli Responsive Materials are specially designed to act upon a specific stimulus. They are able to "feel" their surroundings and *dinamically adapt* their properties upon an external stimulus responding in a functional, predictable and tunable way. May these stimuli be temperature, pH, electric current, magnetic field, pressure, etc. The inclusion of biodegradable, biocompatible semicrystalline polycaprolactone (PCL) backbone in the synthesis of a POSS-based (PolyhedralOligomeric Silsesquioxane) polyurethane (PU), helps design "green polymers". Smart Biomaterials find applications in a wide variety of areas such as medicine, biology, personal care, food science, materials science, and tissue engineering. It is in the scope of this work to study the shape-memory ability of 2 synthesized series of PU that incorporate POSS moiety to improve thermal properties and induce phase separation.

Methods: All reagents, unless specified otherwise, were purchased from Aldrich. Two polycaprolactone diols, 2,000 and 3,000 g/mol, *N*-Methyldiethanol Amine and Hexametilendiisocianate were used in the synthesis of the two series of polyurethanes. A tin(II) 2-ethylhexanoate catalyst was also used and kept under nitrogen. TMP diolisobutyl-POSS", hereafter referred to as POSS diol, was purchased from Hybrid Plastics as a pure (>99%) crystalline solid. A series of POSS-PCL PUs of varying molecular weight were synthesized and collected as highly viscous and transparent liquids. DSC, GPC and TGA data is summarized in **Table 1**. The samples are named PU2/3K_1225, PU2/3K_1326, PU2/3K_1427, where the digits indicate the feed molar ratios of PCL diol, POSS diol, *N*-MEDA and HDI respectively. Calculation of the number of *N*-MDEA units per polymer chain was achieved via NMR peak integration. The thermal transitions were determined by differential scanning calorimetry (DSC) using the Q200™ calorimeter (TA Instruments, Newcastle, DE, USA). The thermal transitions were determined at 20 °C/min. The decomposition temperatures, T_{dec}, were determined by thermogravimetric analysis (TGA), scanning at 20 °C/min, using the Q500 analyzer (TA Instruments, Newcastle, DE, USA). The thermal scans were carried out under dry nitrogen atmosphere. Two-dimensional X-ray diffraction patterns were obtained using a 3-pinhole collimation S-Max3000 WAXS/SAXS system manufactured by Rigaku. Wide-angle X-ray scattering (WAXS) patterns were recorded using a flat-plate camera and Fuji image plates; a sample-to-detector distance of 6 cm was used and the exposure time was set to 40 minutes. The patterns were analyzed using the X-raysoftware POLAR™ v2.6 (Stonybrook Technology Inc., NY, USA).

Sample	M_w	M_w/M_n	T_m	ΔH_m	T_c	ΔH_c	T_{dec}
	(g/mol)		(°C)	(J/g)	(°C)	(J/g)	(°C)
2K_1225	76,600	1.6	128	2.8	116	2.2	282
2K_1326	32,900	1.8	129	3.4	122	2.3	284
2K_1427	92,000	1.7	128	4.8	117	2.0	285
3K_1225	60,700	1.5	33,126	13.5,2.6	119	2.2	280
3K_1326	130,700	1.2	31,127	10.1,2.7	115	2.1	286
3K_1427	73,100	1.2	27,126	2.0,3.7	118	2.5	292

Table 1. Summary of properties of PU2K and 3K systems

Results TGA data demonstrates good thermal stability for 2K and 3K series compared to neat PCL and as predicted by the inclusion of POSS. Two endothermic peaks in DSC show that POSS induces phase separation and this is evident for PU3K series. ΔH_{PCLm} and ΔH_{POSSm} values vary inversely depending on the amount of POSS present in the sample and the M_w of PCL so that as POSS content increases ΔH_{PCLm} decreases. X-ray studies performed at wide and small angle, show that dispersion of POSS across the polymeric matrices allow for the formation of ordered structures. DMA analysis correlates well with the data obtained from DSC, SAXS and WAXS.(**Figure 1**)

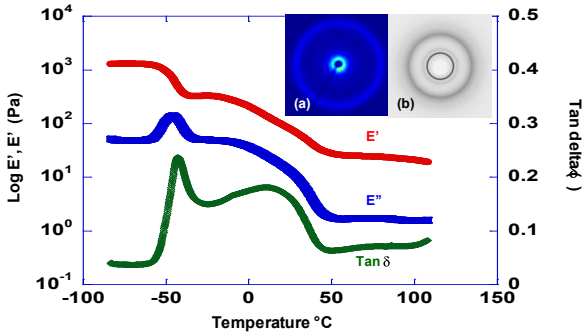

Figure 1. DMA graph for PU3K_1225 showing a rubber like plateau for G'. (a) SAXS pattern and (b) WAXS reflections for for PU3K_1225

Conclusions: We have carried out the synthesis of a series of new PU varying the Mw of the organic PCL backbone and POSS contents. We have fully characterized these materials using thermal analysis (TGA and DSC), GPC and NMR. We have studied the micro and nanostructure using Wide and Small Angle Xray Scattering and testing the SM response based on DMA data.

References: -(Anna M. U. and Marek W. U. *Stimuli-Responsive Polymeric Films and Coatings,* Chapter 1, 2005, pp 1-25)
-(Sedat G.,Sadhan C. J. J. nanosci. Nanotechnol. 2008: 8:1616-1637)