

Summary

Polyurethanes are block copolymers consisting of the so called soft segments, typically a macrodiol and the hard segments. Hard segments exhibit a tendency to aggregation, thus the material has a final morphology of hard domains dispersed in a soft phase (microphase separation). Polyhedral Oligomeric Silsesquioxanes (POSS particles) are the smallest possible form of Silica and their chemical structure facilitates, upon proper modification, their chemical incorporation in the chemical structure of a polymer. This dissertation deals with the procedures by which POSS particles affect the molecular mobility, the microphase separation and the crystallinity of the soft phase of a polyurethane when incorporated in its hard segments.

Materials under investigation were three polyurethanes differing in molecular weight of the hard and soft segments and their composites with POSS incorporated by two kinds of bonds (urethane and urea). The most technologically important and interesting phenomena in polyurethanes are related to the soft phase, so the corresponding macrodiols which were used as soft segments are also studied for comparison.

The matrices are common polyurethanes with polytetramethylene-ether-glycol PTMEG of three different molecular weights (1000, 1400, 2000) as soft phase. Hard segments are sequences of methylene-bis-diisocyanate (MDI) and butanediol. All matrices have 1:1 mass ratio of hard and soft segments, so the average molecular weight of the hard segments is always expected to be the same as that of the macrodiol. POSS particles with a double OH functionality in one of their vertices (PHIPOSS) were incorporated by urethane bonds in the polyurethane chain, by proper substitution of butanediol forming materials with POSS content up to 10wt%. Similarly POSS particles with double amine functionality (DIAPOSS) in one vertex were incorporated in the matrices to form hybrid materials with up to 6 wt% loading.

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were employed to study the morphology of the materials. Thermal glass transition and crystallinity of the soft phase were studied by conventional differential scanning calorimetry (DSC). More information on those phenomena as well as on the microphase separation and the thermal stability was obtained by means of temperature modulated differential scanning calorimetry (MDSC). Molecular mobility (dynamic glass transition and local dynamics) were studied in detail by thermally stimulated depolarization currents (TSDC) and in a broad temperature and frequency range by means of dielectric relaxation spectroscopy (DRS).

Morphology Materials under investigation are porous. Most of the material is organized in spherical structures with diameters of the order of μm . According to literature these spherical structures have a dendroid backbone consisting of hard segments, covered by the soft phase. The spherical structures are larger in the materials with smaller segments presumably because of better mobility of small hard segments and closer distance between them. Incorporation of PHIPOSS reduces the size of the structure while incorporation of DIAPOSS suppresses them for materials with segments with molecular weight 1000 but enhances them in the materials with longer (MW=2000) segments.

Nanoparticles exhibit a tendency to crystalize/aggregate, which is more prominent in

materials with shorter segments. The aggregates/crystals have different morphology, depending on the type of POSS (PHIPOSS, DIAPOSS) and are typically developed mainly within the pores.

Local relaxations Two secondary relaxations are observed with the dielectric techniques in all materials under investigation.

Local γ relaxation is attributed to the crankshaft motion of methylene sequences along the macrodiol chain contour. For all materials it exhibits Arrhenius behavior with preexponential factor $f_0 \approx 10^{15}$ Hz and activation energy $E_{act} \approx 0,4$ eV.

β relaxation of the polyurethanes and the hybrids is attributed to the relaxation of carbonyl groups of the urethane bond with attached water molecules. The β relaxation of macrodiols is attributed to motions of OH terminal groups. For all materials, it is observed by TSDC in the vicinity of -120°C . No variation is observed on its molecular mobility in the polyurethanes and the hybrids and it follows an Arrhenius behavior with preexponential factor $f_0 \approx 10^{16,5}$ Hz and activation energy $E_{act} \approx 0,6$ eV. For macrodiols a deceleration of its dynamics with increasing molecular weight is observed as evidenced by reduction of its peak frequency in DRS spectra and the increase of the temperature of the TSDC peak.

Glass transition The glass transition temperature of the neat macrodiols is not altered significantly in the studied molecular weight range. As evidenced by MDSC and TSDC it has a value $\approx -80^\circ\text{C}$. This is not the case for the glass transition of polyurethanes. The matrix with long ($M_w = 2000$) segments has glass transition temperature only a few K higher than the macrodiols, which suggests that soft segments are well separated by the hard ones. With decreasing molecular weight of the segments, the glass transition temperature, T_g increases significantly (by about 30 K for segment M_w 1000). This happens because shorter segments are expected to dissolve more easily in the soft phase and thus contribute to the glass transition and decelerate it.

The molecular mobility of the polymeric chains is further slightly decelerated by incorporation of PHIPOSS, as evidenced by the increase of T_g upon addition of particles by a few K as compared to the respective matrices (≈ 7 K for 10 wt% loading). This deceleration could be either due to direct polymer particle interaction or the change in micromorphology (higher degree of mixing) and thus indirect deceleration of dynamics.

Broadband dielectric spectroscopy, besides the primary α relaxation, which is connected to the dynamic glass transition, revealed the existence of an α' relaxation, slower than α . α' was attributed to decelerated segmental dynamics of the chains close to hard structures or soft chain crystallites (wherever they are observed). No evidence was provided for alteration of α' neither by the molecular weight of the segments, nor by incorporation of particles. The time scale of α relaxation followed the trends observed by DSC and TSDC, being significantly slower with decreasing molecular weight and further slightly decelerated with addition of POSS.

Incorporation of DIAPOSS causes a significant increase of the glass transition temperature for the material with short segments (by ≈ 15 K for 4 wt% loading), however, DRS revealed that this is not due to the deceleration of α relaxation but rather due to increase of the strength of the α' relaxation. For the matrix with longer segments, there is also an indication of slight reduction of T_g (by 1 – 2 K) due to slightly enhanced microphase separation.

Soft phase crystallinity As observed with MDSC, all macrodiols are semicrystalline with degree of crystallinity in the range 45 – 50%. Crystal structures are more stable and homogeneous in macrodiols with higher molecular weights. PTMEG as part of a polyurethane structure may crystallize, only if its chain is long enough to fold and form the crystal structure. This was only observed for $M_w = 2000$. Moreover, the crystallization was observed only during heating of the material (cold crystallization), suggesting that the nucleation phase is initiated only upon cooling below the glass transition temperature. Addition of PHIPOSS (with urethane bond) hinders crystallization (by about 70 % for 8 wt% loading), this is

considered an indirect effect of increased microphase mixing. On the contrary, DIAPOSS (incorporated by urea bond) enhance the crystallinity as a result of increased microphase separation. Representation of dielectric loss data on dielectric maps (contours of equal dielectric loss on the Arrhenius plane), proposed in this Thesis, suggested the existence of a relaxation mechanism with time scale similar to that of the α relaxation of the neat macrodiol. This observation suggests that domains pure in macrodiol are formed in the material, which are then able to crystallize.

Microphase separation MDSC suggested that the temperature width of the glass transition step, becomes systematically higher with decreasing molecular weight of the segments. For the materials with short segments ($M_w = 1000$) it was further increased by addition of PHIPOSS. A less prominent but observable increase was observed for the other two matrices upon incorporation of PHIPOSS. The glass transition temperature width is a measure of the heterogeneity of the soft phase. In that sense, our observations are compatible with the hypothesis that shorter hard segments are more likely to mix with the soft phase. Also, PHIPOSS reduce the microphase separation of the matrices with more prominent effect on materials with short segments.

The aforementioned observations are also compatible with the width in the frequency range of the α relaxation as observed by DRS.

Maxwell-Wagner-Sillars (MWS) relaxation observed by TSDC, reflects the depolarization of charge carriers trapped at the interfaces of areas with different conductivity. Its temperature difference from the segmental α relaxation is a measure of the distance between interfaces and thus the microphase separation. The results confirm the observations by MDSC (temperature width of glass transition) and DRS (frequency width of α relaxation).

The study of endothermic microphase mixing peaks at high temperatures (50–250 °C) by MDSC reveal that longer (of higher molecular weight) hard segments have a stronger tendency to aggregate/crystallize than the smaller ones and tend to form more stable structures. Addition of PHIPOSS tends to disrupt this aggregation/crystallization.

Incorporation of DIAPOSS increases the width of the glass transition step in MDSC, however, this is due to the increase of strength of the α' relaxation, and not the change in micromorphology as evidenced by the other two criteria (α and MWS peak temperature difference as observed by TSDC, and width of α relaxation peak as observed by DRS). For the materials with longer segments only a small increase of width is observed. Also, for materials with long segments, the hard structures (aggregates/crystals) tend to be more stable with addition of PHIPOSS, presumably due to the enhanced tendency of the urea bond for hydrogen bond formation.

Thermal stability MDSC thermograms at temperatures higher than 250 °C confirmed enhancement of thermal stability upon addition of PHIPOSS which was observed in a parallel work with thermogravimetric analysis. No similar effect was observed upon addition of DIAPOSS.

From all aforementioned observations, it is concluded that POSS particles have a significant hindering effect on the long range order of polyurethane matrices, however their effect in molecular mobility is rather small. The mild deceleration of dynamics is a combined effect of hindering of microphase separation (phase separation in the nanometer scale) and the direct POSS-chain interaction. In the case of incorporation by urethane bond (PHIPOSS) the first mechanism is dominant for materials with low molecular weight of the segments while the second becomes more significant as molecular weight of the segment increases. In the case of incorporation by urea bond, it is the effect on micromorphology which mainly controls the molecular dynamics, for all matrices.