

ABSTRACT

This thesis explores the following aspects on polyurethanes namely: (a) Bulk and surface transitions when castor-oil is gradually substituted in place of a synthetic model hydroxyl component (hydroxyl terminated polybutadiene)(b) Elucidation of solvent interaction with castor oil generated PU network (c) Elucidation of toluene transport through PU-clay nanocomposite followed by effect of other common solvents on segmented morphology of nanocomposites (d) Investigation of wetting effects on segmented morphology of polyurethanes. The findings under these sections are described in chapter 2-4.

In chapter 2 (Investigation of transition in bulk, surface and alterations in block heterogeneities upon solvent interaction in castor-oil co-generated model polyurethane networks),the phase segmentation of A-B blocks with increasing concentration of castor-oil in the PU network is investigated. With increasing castor oil concentration, the radius of individual hard B blocks as well as overall degree of phase segmentation between A-B blocks increased. A bimodal distribution in size of free volume hole radius was noticed in all networks and the size of bigger free volume hole radius decreased with an overall increase in fractional free volume. The bi-soft segments phase mixed with each other and decreased the overall crosslinking density of the network. An overall increase in carbon percentage compared to nitrogen at the surface indicated segregation of soft polyol chains towards the surface of castor oil generated PU network. The soft segments where composed of both butadiene and castor-oil generated urethane chain segments and the overall adhesiveness of the polymer increased. Higher concentration of castor oil on the surface of PU networks decreased the phase shift between A-B segments. The interaction of the PU networks with solvents like tetrahydrofuran, toluene and benzene decreased the existing phase segmentation between A-B blocks with a concomitant increase in radius of

hard B blocks. The hard-hard interaction increased in hexane and DMF and overall degree of phase segmentation decreased slightly compared to THF, toluene and benzene. The equilibrium swelling ratio of PU networks upon its interaction with solvents namely (toluene, benzene and THF) were larger compared to hexane and DMF.

In chapter 3(Effect of solvent interaction on block heterogeneities and filler dispersion in polyurethane-clay nanocomposites) anomalous transport of toluene was noticed in PU clay nanocomposites in contrast to the free volume and tortuous path theories. This phenomenon was attributed to differential interaction of solvent in this multicomponent system. The transient effect of solvent (toluene, benzene, tetrahydrofuran, hexane and dimethylformamide) interaction on segmented block morphology and filler dispersion in nanocomposites was further explored. The SAXS analysis revealed increase in size of hard B block with time upon solvent interaction. At the highest duration of solvent (THF, Toluene, Benzene, and DMF) interaction the parent hard assemblies of nanocomposites having (3% and 5%) clay concentration underwent de-clustering into individual hard B blocks. Formation of ‘splinter’ assembly by breakage of parent hard assembly and swelling of splinter assemblies were noticed at shorter time intervals (15 min, 30min, 45 min) of solvent interaction in all nanocomposites. With increasing time of solvent interaction, the interlamellar d_{001} spacing of intercalated nanoclays increased and its volume fraction decreased in tetrahydrofuran, toluene and benzene compared to hexane and dimethylformamide.

In chapter 4(Wetting influence on block heterogeneities of segmented diblock polyurethanes) we quantified several parameters related to phase segmentation of class of polyurethane induced by surface and subsurface wetting. Wetting decreased the degree of phase segmentation in polyether-based PU foam and polyester based TPU, while it increased in

polybutadiene-based PU coating. Wetting caused swelling of individual hard B block as well as de-clustering of parent assembly in PU foam and TPU. Hard B block swells but de-clustering of assembly was not noticed in PU coating which implies that wetting dynamics is system dependent.

Key words: Bio-renewable resources for polyurethane; PU network; bi-soft segments; segmental dynamics; A-B block segments; sub-nanosopic free volume; surface elemental transition; spluttering; binding energy; dangling chains; segmented phase transitions; domain distribution; degree of phase separation; fraction of microphase mixing; fraction of intersegment mixing; fractional free volume; surface adhesive force; surface energy; subsurface; phase shift; phase mixing; de-clustering; splinter assembly; parent assembly; alteration in individual hard B block and hard assemblies; alpha relaxation of chain segments; solvent transport; barrier properties; solvent interaction; multi-component systems; diffusivity coefficients; equilibrium swelling ratio; tortuous path theory; hydrophobic and hydrophilic chain segments; solubility parameter; clay intercalation; nanoclay dispersion; intradomain stickiness factor; scattering contrast; wetting; thermodynamic compatibility; mesostructure; intersegment interaction; interfacial regions; hard-hard interaction.