

Synthesis and Characterization of Poly(urethane-imide) POSS Nanocomposites

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ABSTRACT

A set of poly(urethane-imide)POSS (PUI-POSS) were prepared by the simple condensation reaction of Isocyanate terminated polyurethane (PU) prepolymer and anhydride terminated polyimide (PI) prepolymer with the evolution of carbon dioxide ceased. The PU prepolymer was prepared by the reaction of PDMS-OH, Cy-POSS and hexamethylene diisocyanate (HMDI). The PI prepolymer was prepared by the reaction of HMDI and dianhydride. Changing the ratio of the PI and PU precursor resulted in a change of the properties of the PUI-POSS polymers from plastic to elastomer. The PUI-POSS were characterized by ATR-FTIR, TGA, AFM, TEM and XRD analysis. ATR-FTIR analysis confirmed the formation of PUI-POSS *via* a reaction between -NCO of PU and -anhydride of PI. The thermal stability of the PU was found to increase by the introduction of imide component. The introduction of the PI component into PUI by condensation reaction method is an effective way to improve the thermal stability. The morphology study was carried out using AFM, TEM and XRD.

Keywords: poly(urethane-imide)-POSS, membranes, nanocomposites.

1 INTRODUCTIONS

Polyurethane (PU) is a one class of polymer that is becoming increasingly important as engineering materials in various areas of industry such as construction, automotive, vehicles, medicine etc., and in many household appliances. PU has excellent properties of both elastomers and plastics, such as high abrasion resistance, wearability, chemical resistance, and high impact strength. However, it is well known that conventional PU materials exhibit poor heat resistance, for example, the acceptable mechanical properties (strength, modulus, etc.) disappear above 80–90°C and thermal degradation occurs above 200 °C, which has limited its application.

The thermal stability and mechanical properties of PU elastomers can be improved by various methods, among them chemical modification of PU structure by introducing into the backbone thermally stable heterocyclic groups [1]. Polyimide (PI) was an important class of heterocyclic polymer with remarkable resistance to superior mechanical, durable, high thermal stability, and good dielectric properties [2,3]. The incorporation of imide group as hard segments in polyurethanes has been successfully

accomplished and their bulk properties have been reported [4]. The incorporation of nanosized POSS macromer into polymers has produced significant improvement in thermal and oxidative resistance as well as in reduction of flammability. The formed PUI systems were being used as a suitable candidates in high-temperature and fire-resistant applications.

The POSS cages become cross-linking points in the network if the multifunctional POSS molecules are used as nanosized fillers in the molecular building-block approach to the design of organic-inorganic hybrid materials. Due to stronger interfacial forces of attraction between the nanometer-sized domains, hybrid formulations exhibit better properties, such as improved thermal stability [5,6], mechanical [7] barrier properties [8], decreased thermal conductivity, reduced flammability [9,10], improved corrosion resistance [11] and reduced solvent (or water) absorbance than those of conventional polymers.

2. MATERIALS AND MEASUREMENTS

Poly(dimethylsiloxane)bis(hydroxyalkyl)terminated ($M_n=5,600$), Hexamethylene diisocyanate (HMDI), 3,3',4,4'-Benzophenonetetracarboxylic dianhydride and dibutyltindilauate (DBDTL) were purchased from Sigma aldrich chemicals. Tetrahydrofuran and N-methyl-2-pyrrolidone were purchased from Rankem chemicals and used after distillation.

Attenuated Total Reflectance Fourier transform Infrared ATR-FTIR spectra were recorded using Perkin-Elmer. Thermogravimetric analysis was performed at a scanning rate of 10°C/min up to 800°C under N₂ atmosphere with a TGA Q50-TA instrument. Surface morphology of nanocomposites was studied using a Nanoscope III AFM instrument, in which the commercial tip of Si₃N₄ provided by Digital Instruments and imaging was done in contact mode at room temperature in air. Cantilever length was 200 μm with a spring constant of 0.12 N m⁻¹. Transmission electron microscopy was performed using JEM 200CX (JEOL, Japan) microscope at an acceleration voltage of 100 kV, recorded on a photographic film and digitized with a PC-controlled digital camera DXM1200 (Nikon, Japan). Polymer microstructure was studied by wide-angle X-ray diffraction (WAXD) measurements (Seifert Tso-Debye-flex-2002 instrument operating in normal/transmission mode; Ni-filtered Cu K α radiation (1.54 Å wavelength); for all experiments, the incident beam was normal to the plane of the polymer).

3 SYNTHESIS OF POLY (URETHANE-IMIDE) POSS NANOCOMPOSITE

All reactions were carried out in a two-necked, round-bottom flask equipped with a magnetic stirrer and nitrogen inlet system. The anhydride end-capped polyimide prepolymer was formed through the reaction of 3, 3', 4, 4' benzophenonetetracarboxylic anhydride, HMDI at 100°C for 6 h (A) (Table 1). The isocyanate end-capped polyurethane prepolymer was formed through the reaction of Cy-POSS was synthesized as reported earlier [12], PDMS and HMDI were stirred at RT for 6 h with the addition of 50 ppm DBDTL catalyst (I). Then, isocyanate end-capped polyurethane prepolymer solution was added into the solution (A), the reaction temperature was maintained at 90 C for 6 h as shown in scheme 1. The resulting viscous solution was transferred to Teflon coated petri dish and kept at room temperature for 6 hrs. Then the dried membranes were kept at oven and maintained at 50°C for 7 hrs.

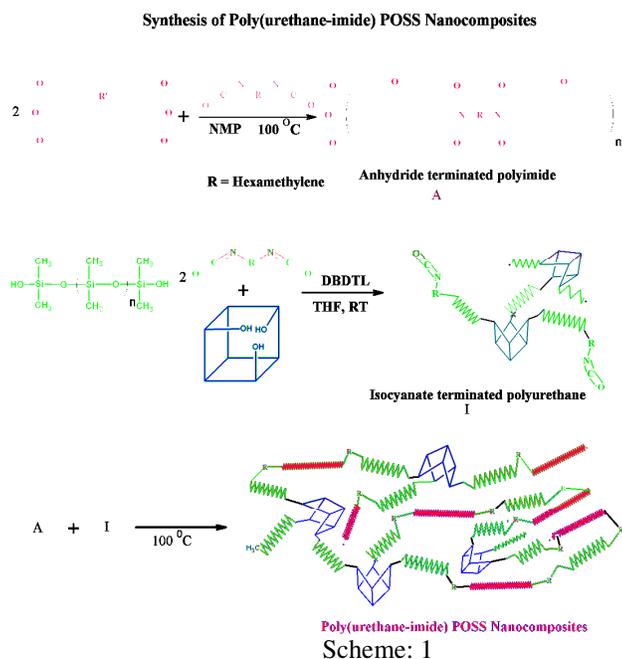


Table 1: Chemical feed composition of PUI-POSS Nanocomposites

S.No	Sample	PU		PI		Cy-POSS
		HMDI	Diol	HMDI	DA	
1	PU	0.55	1.40	-	-	0.05
2	PUI10	0.47	1.40	0.045	0.176	0.05
3	PUI20	0.417	1.24	0.09	0.352	0.05
4	PUI30	0.364	1.08	0.135	0.528	0.05
5	PI	-	-	0.55	1.45	-

4. RESULTS AND DISCUSSION

The structure of these polymers was confirmed by means of ATR-FTIR spectroscopy. In figure 1, the band appeared at 1,760 cm⁻¹ was assigned to the asymmetric stretching vibration of C=O of the imide groups,

characteristic spectral absorbance at 1,385 and 1,244 cm⁻¹ were related to C–N stretching vibration. The bands around 3320–3400 cm⁻¹ are from urethane N–H stretching and bands around 1610 and 2950 cm⁻¹ were duo to aromatic ring stretching vibrations and methylene stretching bands, respectively confirming that the heterocyclic imide rings were successfully incorporated into the polyurethane backbone. In figure 1 it was observed that the intensity of transmittance increase with increasing the amount of imide unit in the PU to PUI30.

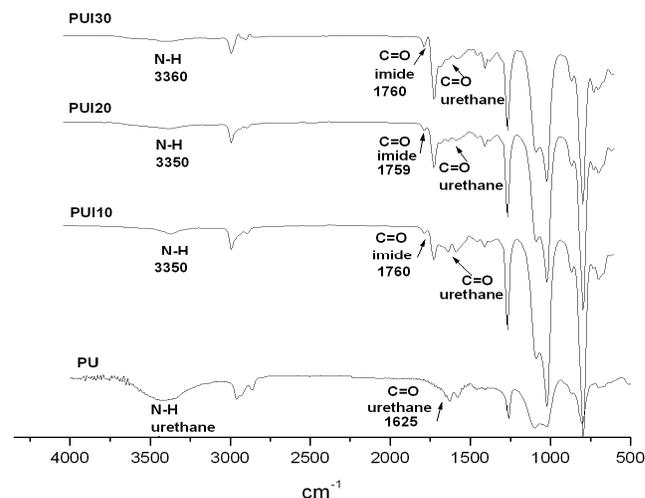


Figure 1: ATR-FTIR of PUI-POSS Nanocomposites

4.1 Thermal property

The thermal stability of the poly(urethane-imide) membranes were measured by thermogravimetric analysis (TGA) at a heating rate of 10°C/min shown in figure 2. Pure polyurethane exhibited 50% weight losses temperature was 443 °C. With the increase in PI content, 50% weight loss temperatures of the poly(urethane-imide) membranes increased from 443°C to 492°C. Compared to pure polyurethane, poly(urethane-imide) membranes exhibited better thermal stabilities due to the presence of the heterocyclic imide groups without phase separation in poly(urethane-imide)[13]. In general, imide rings are considered to be the most stable units among these linking groups, but urethane groups must be the most labile units and will decompose first to start the initial thermal degradation. Assuming a different stability of the urethane and the imide units, the first stage of weight losses might be attributed to the early degradation of the urethane linkages. The reason for these results could be that the more thermally sensitive PU moiety began to decompose before PI moiety was degraded. The pure PI with a tighter and more rigid coherence between chains possessed a good thermal stability, whereas PUI-POSS (i.e., sample PUI-POSS10 to PUI-POSS30) having a relatively increased the amount of hard segment had less chain coherence because of fewer imide groups in the backbone chains.

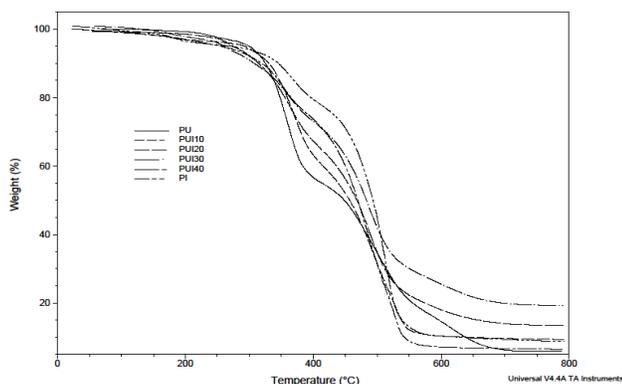


Figure 2: TGA curve of PUI-POSS Nanocomposites

4.2 Surface Morphological studies

The wide-angle X-ray diffraction (WAXRD) measurements at room temperature in the region of $2\theta = 2^\circ$ to 30° were applied to examine the crystalline structure of nanocomposites are shown in figure 3. All the poly(urethane-imide) membranes except POSS exhibited structure less amorphous halo indicating the absence of crystallinity. For comparison, the XRD curve of Cy-POSS, PU and PUI10-PUI30 were also incorporated in this figure 3, which was measured under the identical condition. The diffractogram of the Cy-POSS (e) showed very intense, characteristic POSS crystalline peaks at $2\theta = 16.1$ and $2\theta = 19.3$ indicating that POSS is highly crystalline. The XRD pattern show broad peaks $2\theta = 14.5$ to 17.5 and $2\theta = 20$ to 25 for PU and PI respectively. The intensity of the peak range $2\theta = 20$ to 25 increased with increasing PI loading. It was reported that such two diffraction peaks are due to two different segments in the polymer matrix [14]. With increase in PI contents, PUI membranes were expected to exhibit a new amorphous peak. With increase in PI contents, polymers were expected to increase the intensity of PI peaks.

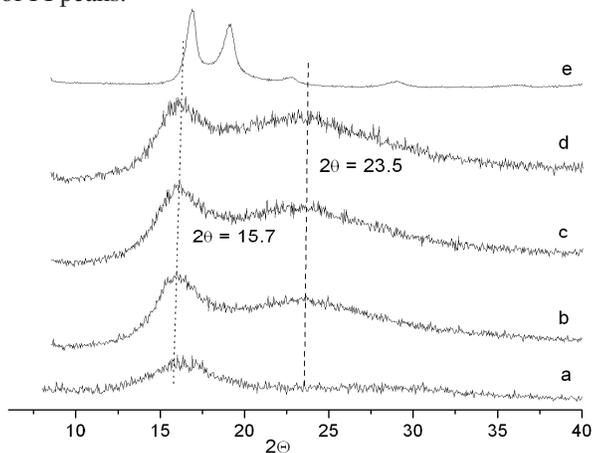


Figure 3: WAXRD curve of (a) PU, (b) PUI10, (c) PUI20, (d) PUI30, (e) Cy-POSS Nanocomposites

The surface morphology and roughness of the formed PI and PUI-POSS hybrid membranes were investigated by AFM (figure 4). In comparison with the PI, PUI10 to PUI30 shows a rough surface for the composite and the formation of a less homogeneous surface. The surface topography, three-dimensional topographical image and phase images are given in figure 4. Similar to the extent of projection of one phase, the surface roughness also increased with increase in the PI content. This further confirmed that the imide content increased the roughness of the surface morphology. It has been reported in the literature that phase separation could cause surface roughness. Therefore, this could be attributed to the existence of non-compatible phases. Similar correlation of surface roughness to the phase separation has been reported for tetramethyl bisphenol A polycarbonate and polystyrene blends [15].

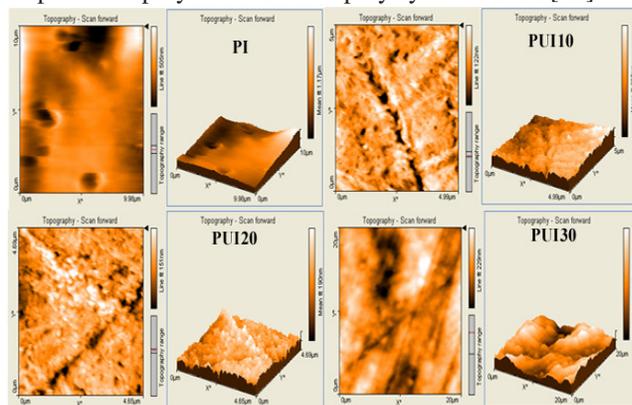


Figure 4: AFM image of PUI-POSS Nanocomposites
The morphology of PUI-POSS was further investigated by TEM shown in Figure 5. It is observed that all the composites were transparent, suggesting that no phase separation occurs on the scale at least more than the wavelength of the visible light. The TEM observes the dispersion of POSS particles in PUI-POSS matrix shown in Figure 5. It is seen that the two-phase morphology with branching strip shaped domain distributes in continuous matrix appears in PUI-POSS.

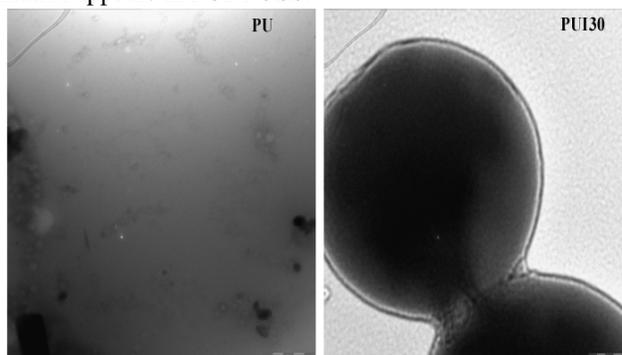


Figure 5: TEM image of PUI-POSS Nanocomposites

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