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Enhanced mechanical properties of polyurethane composite coatings through nanosilica addition

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ABSTRACT

Tin rich surfaces inside Pb-free electronics are more prone to tin whisker growth, thereby resulting in electrical failure of components. Conformal polyurethane (PU) coatings, which can be used as a mitigation strategy for such whisker growth, were investigated in this study. Nanoparticles of silica (~20 nm in diameter) were added via liquid suspension to the PU resin to improve its mechanical properties. Four compositions of functionalized nanosilica suspensions, 10 wt.%, 20 wt.%, 30 wt.% and 50 wt.% (corresponding to the solid silica weight of 3.50%, 6.74%, 9.75%, and 15.17%, respectively) were evaluated to establish the relationship between microstructure developments and mechanical properties. Fourier-transform infrared spectroscopy (FTIR) and low-kV field emission scanning electron microscopy (FE-SEM) were used to examine the effects of nanosilica suspension addition to the PU resin. Mechanical properties of the coating were not only evaluated by nanoindentation for localized PU matrix properties but also by uniaxial tensile testing for composite properties. Results from both scales show that the addition of the particle suspension up to 20 wt.% (corresponding to 9.75 wt.% nanosilica) makes optimum mechanical performance consisting of good modulus, strength and ductility. This conclusion is also supported from microstructural, as well as chemical aspects of the PU coatings with the addition of nanosilica suspension.

1. Introduction

Electronics components and boards which utilize pure tin, tin-rich surfaces and tin-based solders have become more prevalently used these days following the Restriction of Hazardous Substances (RoHS) directives banning the use of lead (Pb) [1]. One issue associated with the increased usage of tin is the appearance of tin 'whiskers' which nucleate and grow from the stressed tin-rich surfaces resulting in metallized surface damage and unwanted debris inside the package, cause current leakage, and may often cause catastrophic failure. Polymer systems such as commercially available parylene-C and other generic polyurethanes (e.g., Arathane 5750$^{\text{TM}}$) have been considered for being used in whisker mitigation coating strategies [2,3]. Nevertheless, these coating techniques tend to be cost prohibitive (in case of parylene-C) and often involve complex processing [4]. A coating technique which is economical and requires relatively simple process parameters is thus desired. In addition, reworkability is another important criterion for these conformal coatings.

Polyurethanes are segmented block copolymers that inherently possess excellent physical properties owing to microphase separation yielding alternating hard (isocyanate) and soft (long chain polyol) segments [5,6]. These features make polyurethanes especially useful as a conformal coating in electronics assemblies besides their versatility in processing, electrical properties, and optical transparency. In addition, efforts in building nanocomposite materials from polyurethanes have been accomplished with relative ease giving way to remarkable increases in their mechanical strength and thermal stability with newer applications including mining and civil engineering where PU composites have replaced more traditional products [7,8]. Previous studies in developing

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nanoparticle polymer composites have looked at different length scales of filler particles [9] and different inorganic fillers [10–12]. However, in an effort to maintain the viscosity and the transparency of the coatings, nano-sized fillers need to be employed. The rheological advantages of incorporating nano-fillers in PU elastomers have been well documented [13]. These filler particles are also expected to contribute to the strength of the matrix due to the composite strengthening effect of the particles in the matrix. Petrovic [14] and others [15–17] have extensively studied the relative advantages of using nano-fillers in a single phase polyurethane. However, in the case of functionalized fillers, as is the case in this study, there is an additional benefit of strong chemical bonding between the particles and the matrix that adds to the overall coating performance. Well functionalized nanoparticles can also reduce the chance for particle agglomeration in the coating. Silane coupling agents (SCA) were utilized to link the native hydroxyl groups available on the surfaces of the nanosilica particles with the PU matrix [18,19].

In this work, isocyanate-functionalized nanoparticles of silica (~20 nm in diameter) in suspension were blended into the polyurethane resin with an expectation to provide mechanical improvement. For this, varying amounts of the additive suspensions were blended with the polyurethane base and the resultant composite coatings were characterized to monitor the mechanical properties of the resultant coating. To separate out the extent of the effect of the nanoparticle addition from that of the isocyanate which is included in the particle suspension, another set of sample with only the isocyanate hardener (without nanosilica particles) was also analyzed.

It was also attempted to determine an optimum concentration of nanoparticle addition that would potentially increase tin whisker penetration resistance, which is selected from coating microstructures and mechanical performance. The mechanical properties of the nanocomposite coatings were evaluated using both tensile testing and nanoindentation, the latter of which allows for extremely localized nanoscale mechanical property tests in the 1–2 μm indentation depth range. Infrared spectroscopy was used to characterize various functional groups that are influenced by the coating synthesis and degradation. Low-kV FE-SEM was used to observe the microstructure developments of the nanoparticle-filled polyurethanes and to examine the distribution of the nanoparticles across the coating thickness. These composite coatings should also have the potential to give a better surface coverage on vertical surfaces by adding the nanoparticles to the PU resin that will in turn provide the enhanced whisker mitigation ability.

2. Experimental techniques

2.1. Materials

Moisture-curable PU coatings using commercially available Hysol PC18M (Henkel Inc., Irvine, CA) mixed with Desmodur XP2742 suspension (Hexamethylene diisocyanate, HDI, trimer with 20 nm mean diameter silica nanoparticles) from Bayer MaterialScience (Pittsburgh, PA) were pre-cast in requisite compositions (Table 1). Hysol PC18M is a single component urethane prepolymer in 2-methoxypropyl acetate solvent (along with xylenes, ethylbenzene, and toluene diisocyanate). Evaporation of the solvent during a curing process in the presence of moisture yields a flexible continuous polymer. The base polyurethane (100% PC18M) was used as the control sample and four nanosilica added resins based on weights of the suspension were prepared and cast as coatings. 10%, 20%, 30% and 50% XP2742 suspensions were blended into PC18M to yield each composition containing 3.5%, 6.74%, 9.75% and 15.17% weight of nanosilica. Further, four more compositions (5.18%, 10.36%, 15.54%, 25.9%) of Desmodur N3300 (Aliphatic polyisocyanate (HDI trimer) only) from Bayer MaterialScience were added to the PC18M to make the same isocyanate contents as in the XP2742 compositions.

Nanosilica particles in the XP2742 suspensions are functionalized with an isocyanate (NCO) that links a bonding between the silica nanoparticles and the polymer matrix when mixed. On the other hand, the N3300 suspension only contains an isocyanate without nanosilica particles. For convenience, in this paper, suspension weights (which includes the solvent, isocyanate, and nanoparticles) of the additives (10%, 20%, 30% and 50%) will be specified in place of the actual filler weights while referring to the nanosilica samples.

2.2. Methods

2.2.1. Sample fabrication of polyurethane coatings

All compositions of the coatings tested were prepared by spreading the corresponding resins as thin coatings on glass substrates or slides. In case of PC18M containing the XP2742 (isocyanate + nanosilica) suspension, the presence of the accompanying isocyanate not only bonds the silica to the polyurethane matrix but also increases the hard segment concentration in PU. During the pre-processing, the blended resins were cast onto glass substrates with the thickness regulated to be less than 100 μm in all cases. The evaporation step was conducted on a hot plate for 1 h at 45 °C followed by curing in an oven regulated at 60% relative

Table 1
List of PU compositions examined in this work.

Sample number	Base polyurethane	wt.% suspension added to base	wt.% of isocyanate in suspension (HDI Trimer)	wt.% of solid nanoparticles (after curing)
1	PC18M*	0%	0%	0%
Nanosilica + Isocyanate(HDI) containing compositions				
2	PC18M	10% XP2742**	5.18%	3.50%
3	PC18M	20% XP2742	10.36%	6.74%
4	PC18M	30% XP2742	15.54%	9.75%
5	PC18M	50% XP2742	25.90%	15.17%
Isocyanate (HDI)-only containing compositions***				
6	PC18M	5.18% N3300	5.18%	0%
7	PC18M	10.36% N3300	10.36%	0%
8	PC18M	15.54% N3300	15.54%	0%
9	PC18M	25.90% N3300-	25.90%	0%

* PC18M contains 50% solvent.
** XP2742 suspension contains 51.8% N3300, 18.3% nanosilica, and 30% butyl acetate solvent.
*** Sample #6, #7, #8, and #9 are a replica of #2, #3, #4, and #5 without nanosilica, respectively.