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Electron beam irradiation effect on the mechanical properties of nanosilica-filled polyurethane films

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ABSTRACT

Polyurethane (PU) is a good candidate to be used as conformal coatings for space electronic components and boards due to its manufacturability and desirable mechanical properties. It also keeps tin whiskers from growing on the tin-rich surfaces under a long-term usage that will ultimately result in electrical failure. PU coating can, however, be susceptible to the irradiation damage in space environment that ultimately alters its chemical structure and mechanical behavior. In this study, four variations of PU-based coatings (PU filled with and without nanosilica particles; polyurethane acrylate (PUA) filled with and without nanosilica particles) were investigated to understand the irradiation damage on chemical structure and the corresponding mechanical properties under three electron beam irradiation fluences (1×10^{14} cm^{-2}, 1×10^{15} cm^{-2}, 1×10^{16} cm^{-2}). Infrared spectroscopy was used to examine the degradation of chemical bonding with irradiation. Microphase separation, the degree of curing, and molecule chain mobility were examined via differential scanning calorimetry (DSC) by monitoring the shift in glass transition temperatures after the irradiation. The electron beam irradiation on PU films resulted in the quinone structure formation whereas, on PUA film, microphase separation increased, thereby making both films stronger and stiffer, but less ductile and more brittle. As a result, PU and PUA coatings under a high fluence of irradiation will be more prone to tin whisker penetration. This study also shows the potential effect of nanosilica on retarding the irradiation damage in PU and PUA films.

1. Introduction

Tin whisker growth leads to high reliability risks among electronic components and boards. One of the effective solutions to solve this issue is to apply a conformal coating, which will mitigate the tin whisker growth by either slowing down the growth rate or blocking the growth at the beginning [1–5]. PU can be a good candidate as a conformal coating due to its affordable process and reworkable capability. PU is a segmented block copolymer with alternating hard (isocyanate) and soft (long chain polyol) parts which are immiscible with each other [6–9]. In addition, its adjustable mechanical properties by having both elastomeric and plastic properties make PU quite adaptable to numerous coating applications [10,11]. In particular, space electronics are exposed to high energy irradiation for an extended period and the subsequent degradation of the conformal coating will add significant concern to the long-term reliability due to its impact on tin whisker mitigation capacity [12].

Our previous studies have focused on the effect of nanosilica addition and various curing conditions on the mechanical properties of PU and PUA coatings [13,14]. However, the polymer degradation under high energy irradiation circumstances has received little attention. Hence, the purpose of this study is to obtain the information of the influence of high-energy electron beam irradiation on the mechanical properties of PU-based films. In this work, four types of films (plain PU, PU with 20% nanosilica suspension, plain PUA and PUA with 10% nanosilica suspension) were investigated to check their irradiation effect. Nanosilica suspension was

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filled with isocyanate-functionalized silica nanoparticles (20 nm in diameter), which are covalently bonded to PU matrix upon curing to improve mechanical properties of the PU and PUA films. According to our previous findings [13], those amounts of nanoparticle suspensions (i.e., 20% and 10%) resulted in the optimum mechanical behavior of PU and PUA coatings, respectively.

The mechanical properties of the electron beam irradiated films were evaluated by tensile testing and microhardness tester. The former test focused on bulk properties while the latter did on localized surface properties. In particular, microhardness test evaluated the resistance of these films on indentation, which can mimic tin whisker penetration phenomenon. Fourier transform infrared spectroscopy (FTIR) was used to characterize the changes in chemical bonds under irradiation, such as bond breaking and oxidation of the film. Further, the microphase separation was examined by differential scanning calorimetry (DSC) through the shift in glass transition temperatures of hard and soft segments [15].

2. Experimental

2.1. Materials

Moisture curable PU resin (PC18M; Henkel Inc., Irvine, CA) and dual curable (by both moisture and UV) PUA resin (PC40UMF; Henkel Inc., Irvine, CA) were used in this study. PC18M is a urethane prepolymer in 2-methoxypropyl acetate solvent (along with small amounts of xylenes, ethylbenzene, toluene diisocyanate, toluene). PC40UMF is a mixture of 1,6-diisocyanatohexane homopolymer, 2-hydroxyethyl acrylate and isobornyl acrylate. The source of nanosilica is from hexamethylene diisocyanate trimer with 20 nm mean diameter silica nanoparticles (Desmodur XP2742 suspension; Bayer MaterialScience, Pittsburgh, PA). 20% and 10% XP2742 suspension were added to PU and PUA to get a composition containing 6.74 wt.% and 1.88 wt.% of nanosilica, respectively.

2.2. Film fabrication and irradiation

Four types of compositions (plain PU resin, PU resin with 20% XP2742, plain PUA, PUA with 10% XP2742) were used to spread the resins as thin film on glass substrates with the help of attached tape at the edge of the substrate to control the thickness of the cast films (around 40–60 μm). For plain PU and PU with 20% XP2742 coatings, they were left for 1 h on a hot plate at 45 °C for the solvent evaporation process after a thin layer of resin was applied, then followed by curing in an oven under the condition of 60% relative humidity (RH) and 60 °C for 4 h. For plain PUA and PUA with 10% XP2742 coatings, the initial solvent evaporation only needed 20 min to remove a small amount of high vapor pressure solvent in the resin, then the dual curing processes were made sequentially by UV light for 20 min and then oven curing with 60% RH and 80 °C for 4 h. The UV power source is a steady-state UV-A (365 nm) SB-100 lamp from Spectroline with intensity of 4800 $\mu W/cm^2$ at a concentrated spot. Finally, the cast films were peeled off from the glass substrates.

The cured films were peeled from glass substrates and cut into a 2.5 in × 3.0 in rectangular shape, which was later treated for electron beam irradiation at Takasaki Advanced Radiation Research Institute. During the experiment, the electrons accelerated at 1 MeV were bombarded on the film samples with three fluences (1×10^{14} cm^{-2}, 1×10^{15} cm^{-2}, 1×10^{16} cm^{-2}) in a nitrogen atmosphere by keeping the current at 1 mA, corresponding to a rate of irradiation of 1.65×10^{12} cm^{-2} s^{-1}. Such an irradiation rate was low enough to prevent an increase of the sample temperature during the electron irradiation since the samples were put on a water-cooled copper plate. The penetration depth of 1 MeV electrons into polymer is on the order of centimeters [16]. This allows the uniform energy deposition through the film thickness of 40–60 μm.

The electron energy (1 MeV) and fluences used in this study were high enough to simulate the radiation resistance of the polyurethane-based conformal coatings in the actual space environment. The criteria for electron energy and fluences had been set by Jet Propulsion Laboratory for the radiation hardness of solar cells in the space application [17]. Moreover, the irradiation under 1 MeV electrons with 1×10^{16} cm^{-2} fluence roughly corresponds to the exposure in geostationary earth orbit for about ten years [18].

2.3. Characterization methods

The chemical structure of the films under various irradiation fluences were characterize by FTIR (Spectrum100R, PerkinElmer), in which the films were tested under attenuated total reflectance (ATR) mode and the scanning wave number range was 600 cm^{-1} to 4000 cm^{-1} with resolution of 2 cm^{-1} and 32 scans. The peaks were indexed in comparison with those from the literature [19]. And all the samples for direct comparisons were tested on the same batch of measurements and compared at the same background level. The status of microphase separation, which has an obvious influence on the mechanical behavior of the films after electron beam irradiation was studied by DSC. The working temperature ranged from −80 °C to +260 °C with a 10 °C/min heating rate. The glass transition temperature obtained by DSC was calculated at the inflection point of heat flow.

The mechanical properties of irradiated films under different irradiation fluences were tested at room temperature by Instron Model 5543 universal testing machine according to a modified ASTM D882 standard used for thin film plastics [20]. The films were cut into a rectangular shape (2 in × 0.5 in). Sample thicknesses were measured by a micrometer. During the test, the sample gauge length was set to be 1 inch and the deformation rate was 0.05 in/min. Stress-strain plots were obtained to identify the tensile strength, elastic modulus, total elongation and yield strength of the irradiated samples. Four tensile specimens per each irradiation condition were measured to get an average value and the corresponding standard deviation. In addition to mechanical properties of the bulk specimens, the surface (localized) indentation behavior also plays an important role in the conformal coating to mitigate the tin whisker penetration. Wilson Vickers Hardness Tester was used to measure the surface hardness of the irradiated samples with a 10 g indentation load for the duration of 10 s. Each irradiated specimen was indented for at least five times to calculate the average and standard deviation.

3. Results and discussion

3.1. Chemical structure characterization

FTIR analysis was used to investigate the effect of high energy irradiation on chemical structure of polyurethane films. Fig. 1 shows the FTIR spectra of PUA films (PC40UMF) under various irradiation fluences. It can be seen that the bond breaking exists during the irradiation, especially for the highest irradiation fluence (1×10^{16} cm^{-2}), reflected by the peak intensity decrease with increasing fluence for some urethane related peaks in the IR spectrum. Both the hard segments and soft segments in PUA were influenced by irradiation, because the peak intensities of C-N (1245 cm^{-1}) and C-O-C (1162 cm^{-1}) bonds decreased with increasing irradiation fluence, respectively. Other urethane related peak intensities also decreased, such as C=O (1730 cm^{-1}), C-O (1050 cm^{-1}), CNH (1528 cm^{-1}) and N-H (1452 cm^{-1}).