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PHYSICO-CHEMICAL, THERMAL AND ELECTRICAL PROPERTIES OF THE FABRICATED POLYURETHANE THIN FILMS UTILIZING BIO-BASED EPOXIDIZED SOYBEAN OIL

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ABSTRACT

We successfully fabricated polyurethane (PU) thin films deposited on glass substrates utilizing bio-based epoxidized soybean oil (ESBO) via spin coating technique. Prior to deposition, one-shot polymerization condensation reaction was made by reacting varied amount of ESBO-based polyols with isocyanate. Visual inspection using stereomicroscope revealed that both petroleum-based and ESBO-based polyols polyurethane exhibit homogeneous and superior quality thin films as confirmed by scanning electron microscope (SEM) images. Furthermore, Fourier transform infrared (FTIR) spectra showed a higher N-C-O vibrational mode transmission for bio-based polyols while lower vibrational mode transmission for petroleum-based polyols. On the other hand,

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FTIR spectra showed a higher O-H vibrational mode transmission for bio-based polyols while lower for the petroleum-based polyols. This phenomenon may trigger a stoichiometric ratio closer to unity between polyols and isocyanate that will significantly produce a homogeneous thin film deposition. Moreover, fabrication of uniform thin films was also influenced by the spin coating speed. The fabricated PU thin films utilizing ESBO-based polyols exhibit a higher thermal stability as indicated in the thermogravimetric analysis (TGA).

Keywords: Polyurethane; epoxidized soybean oil; spin coating; thin films

1. INTRODUCTION

Polyurethane (PU) dominates the polymer industry nowadays due to its wide range of applications. In semiconductor and microelectronics industries, intensive research have been done to integrate polymeric thin films as interlevel dielectric material, stress buffer layers and as encapsulants to chip-scale and wafer-level packaging in ultra-large-scale-integration (ULSI) devices [1]. Silicon dioxide is usually utilized as dielectric material having a dielectric constant of 4 [2][3]. Due to the miniaturization of integrated circuits (IC) in order to address the demand of high speed computers, lower dielectric constant materials are indispensable.

One of the candidate materials having much lower dielectric constant is polymer. In fact, a highly fluorinated polyimide material was used as dielectric material which exhibit a dielectric constant lower than 2.3 [4]. However, this material has inadequate thermal stability that failed to address the demand in IC integration. Furthermore, this material can cause dramatic concern for the presence of fluoric acid evolution during its processing that may cause harmful corrosive effects to the fabricated IC. Alternative material with lower dielectric constant has been currently explored by incorporating a hybrid poly(ethylene oxide)-polyhedral oligo-silsesquioxane (PEO-POSS) template into the polymer matrix [5]. However, it requires a higher reaction temperature which is not suitable for IC production. There was also an attempt to utilize photosensitive poly-p-phenylene-benzobisoxazole (PBO) thin film utilized as dielectric material for heterojunction bipolar transistor [6]. However, complex synthesis processes in film production makes it difficult for IC integration. It is noteworthy that these polymeric materials with low dielectric constant may pose long-term environmental and waste management problems due to the utilization of petroleum-based as raw material. In this regard, renewable and sustainable raw materials in order to fabricate interlayer dielectric are currently explored.

Bio-based polymers are good candidates to possibly replace the petroleum-based polymers with similar physico-chemical, thermal and electrical properties. Tailoring the thin film properties may be done by changing the polymeric composition [7][8]. Homogeneity and superior quality of the deposited thin films are among the criteria for IC production. Furthermore, uniform, even and full substrate thin film coverage as well as no spillage on the edge of the substrate is highly desirable in thin film deposition.

There were no reports on the utilization of bio-based polymers in fabricating thin films for lower dielectric materials. In this work, we fabricated polyurethane thin films utilizing bio-based epoxidized soybean oil (ESBO) as replacement in the petroleum-based polymer production. Characterization on the physico-chemical, thermal and electrical properties of the fabricated thin films was investigated.

Experimental Details

Substrate cleaning: Glass slide was used as a substrate. Ultrasonic cleaning and subsequent acetone, ethanol and 1M HCl standard cleaning process was carried out in order to remove impurities in the substrate and finally washed with distilled water and dried at ambient conditions.

PU formulation: Polyurethane was produced via one-shot polymerization using hand mixing method of A-side and B-side materials. The A-side component consists of polymeric methylene diphenyl diisocyanate (MDI). On the other hand, the B-side consists of polyols. We utilized petroleum-based polyols (VORANOLTM 490), 50% ESBO replacement polyols and 100% ESBO replacement polyols. No catalysts, surfactant and blowing agent were used.

Thin film deposition: Spin coater was used at different speed (2000, 4000 and 6000 rpm) during PU thin film deposition for 30 seconds. Dropwise method utilizing the completely mixed PU was done on the glass substrate. Subsequent curing of the deposited PU thin film was carried out using oven at 150°C for one hour.

Characterization techniques: The deposited PU thin films on glass substrates were characterized using stereomicroscope and scanning electron microscope (JEOL JSM-6510LA) to investigate the surface morphology. Fourier transform infrared spectroscopy (Perkin Elmer

Spectrum 100) was used to examine the vibrational modes of the functional groups present. Thermo-gravimetric analysis (Shimadzu DTG-60H) was performed to investigate the thermal stability of the deposited PU thin films. Moreover, current-voltage measurements (National Instruments I-V tracer) using two-point probe method was used to determine the electrical resistance.

2. RESULTS AND DISCUSSION

Figure 1 shows the stereomicroscope images of the PU thin films with ESBO bio-based replacement and petroleum-based polyols deposited at different speed. It is very remarkable that the 100% ESBO replacement at 6000 rpm deposition [Figure 1(g)] showed a homogeneous and uniform PU thin film which is comparable to the 100% petroleum-based polyols. On the other hand, lower deposition speed (2000 and 4000 rpm) utilizing 100% ESBO replacement and 50% ESBO replacement as well as the 100% petroleum-based polyols produced inhomogeneous and non-uniform PU thin films. It is also observed that edge spillage did not occur at 100% ESBO replacement which is comparable to the 100% petroleum-based polyols. All other deposited thin films were suffering from edge spillage effect.

The quality of the deposited PU thin films is also influenced by the deposition speed similar to the previously reported results [9][10]. It is also observed that at 6000 rpm, highly uniform and evenly distributed thin film was produced. On the other hand, lower rpm would result to inhomogeneous and uneven thin films maybe due to the dropwise method that will not completely mixed the PU during spinning and will dried up before it spread the entire substrate. Thus, 6000 rpm may be suggested as the optimum spinning speed to produce a highly uniform and even PU thin film.

Figure 2 showed the scanning electron micrographs of the deposited PU thin films on glass substrate. It is very apparent that 100% ESBO replacement revealed a highly uniform, deposited thin film [Figure 2(a)] as compared to the 100% petroleum-based polyols. The 100% petroleum-based polyols exhibit bubble-like structures which consequently made the surface uneven. On the other hand, the 50% ESBO replacement showed a uniform deposition but in larger scale, inhomogeneity was observed as shown in Figure 1(h). Debris observed in the 50% ESBO replacement shown in the SEM image in Figure 2(b) can be attributed to the glass fragments during sample cutting.

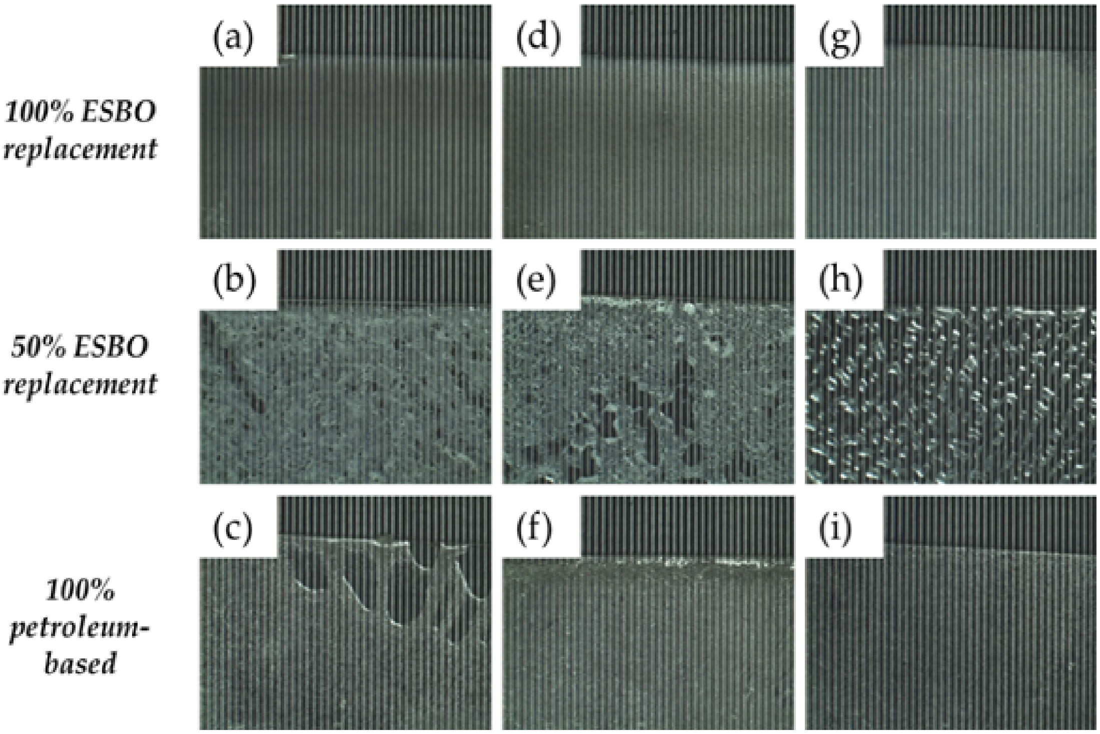

Fig.1. Stereomicroscope images of the deposited PU thin films on glass substrate with 100% ESBO replacement, 50% ESBO replacement and 100% petroleum-based polyols deposited on glass substrate at different speed (a,b,c) 2000 rpm, (d,e,f) 4000 rpm and (g,h,i) 6000 rpm.

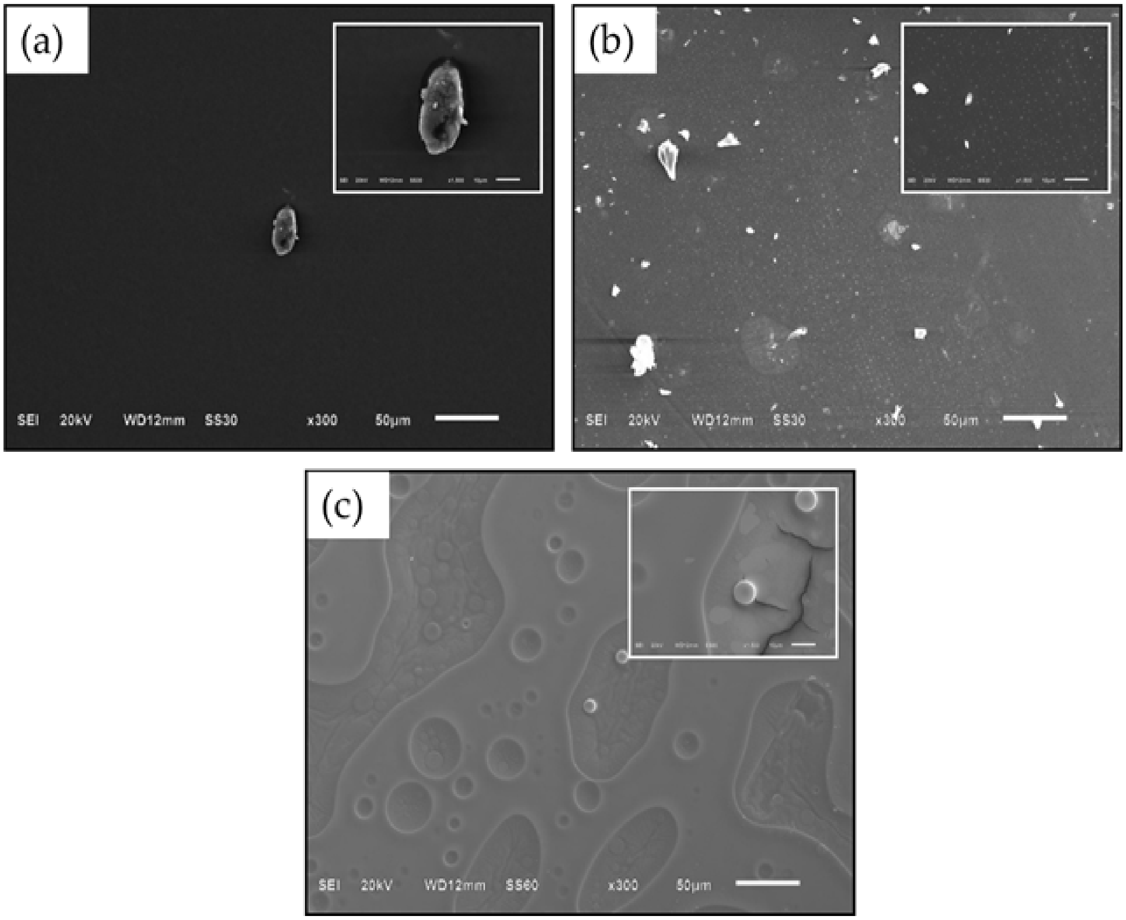

Fig.2. Scanning electron micrographs of the deposited PU thin films on glass substrate with (a) 100% ESBO replacement, (b) 50% ESBO replacement and (c) 100% petroleum-based polyols.

In order to determine the functional groups present in the deposited PU thin films, FTIR spectroscopy was carried out over the range of wavenumbers 650 cm^{-1} - 4000 cm^{-1}. Figure 3 revealed the FTIR spectra of the PU thin films with 100% ESBO replacement as well as the petroleum-based polyols. The broad band around 3195 cm^{-1} and 3414 cm-1 can be associated to O-H and N-H stretchings. It is observed that higher transmittance occurred with 100% ESBO replacement was done as compared to the 100% petroleum-based polyols. On the other hand, the intenseband around 2275 cm-1 can be assigned to NCO stretching. It is noteworthy that the transmittance for the 100% ESBO replacement is higher as compared to the 100% petroleum-based polyols. This phenomenon might maintain the stoichiometric ratio of O-H and N-C-O closer to unity in order to produce highly uniform and evenly distributed PU thin films as shown in Figure 1(g) and Figure 1(i). The signature bands comprising the functionalities of the PU thin films can be found between 1230 cm-1 to 1742 cm-1 which are attributed to C=O stretching, aromatic C=C, C–C stretching, C–N stretching, C–O–C stretching, C–O stretching, N-H bending, C-H bending, C-H wagging, O-H bending and C-H rocking vibrational mode suggesting that we have successfully deposited PU thin films on glass substrate similar to the previously reported vibrational modes [11][12]. The competition of O-H and N-C-O stretching is very essential in PU formation and the stoichiometric ratio must be maintained closer to unity in order to produce a high quality PU thin film [13].

In order to determine the thermal stability of the deposited PU thin films, thermogravimetric analysis (TGA) was carried out. Figure 4 showed the TGA spectra of the deposited PU thin films with 100% ESBO replacement and 100% petroleum-based polyols. It is observed that temperature between 24°C to 100°C corresponds to the moisture removal of the deposited PU thin films. It is very apparent that the onset of degradation for hard segments is higher (~215 °C) for 100% ESBO polyol replacement PU thin film as compared to the onset of degradation for hard segments for the 100% petroleum-based polyols (~110 °C) suggesting that 100% ESBO replacement will have a higher thermal stability. Lower onset of degradation for soft domains (~320°C) was observed for 100% petroleum-based polyols while 490 °C for 100% ESBO replacement. This thermal stability for 100% ESBO replacement is a good potential for the realization of bio-based polymer for interlayer dielectric application with higher thermal stability.

The calculated resistances of the deposited PU thin film with 100% ESBO replacement at different voltage limits at current limit of 0.1 A and 0.001 A are shown in Figure 5. It is observed that linear increase occurred as the voltage limit increases. The calculated resistance is comparable with the reported resistance of the low dielectric polymers [14][15]. This result might be a good start to consider PU thin films utilizing bio-based polyols as an alternative low dielectric constant material.

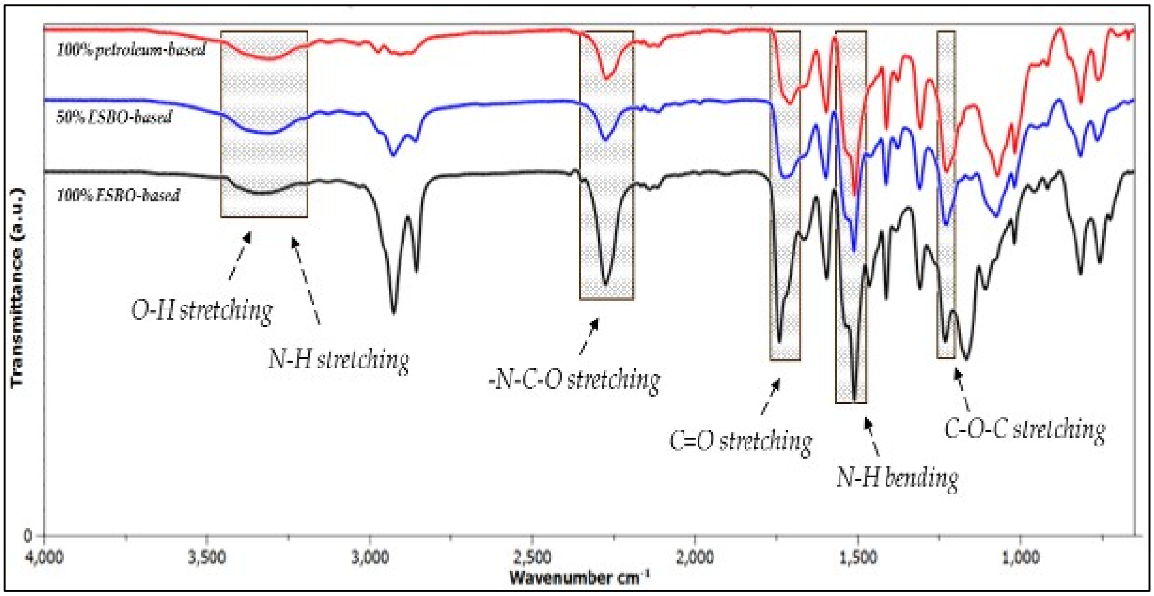

Fig.3. Fourier transform infrared spectra of the deposited PU thin films on glass substrate with 100% ESBO replacement, 50% ESBO replacement and 100% petroleum-based polyols.

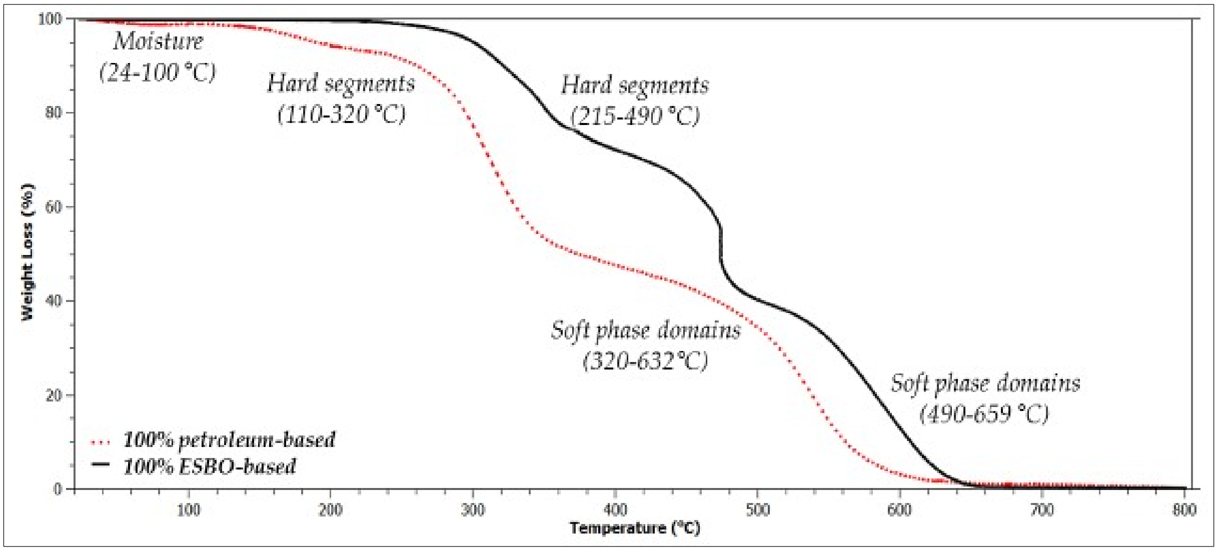

Fig.4. TGA spectra of the deposited PU thin films with 100% ESBO replacement and 100% petroleum-based polyols.

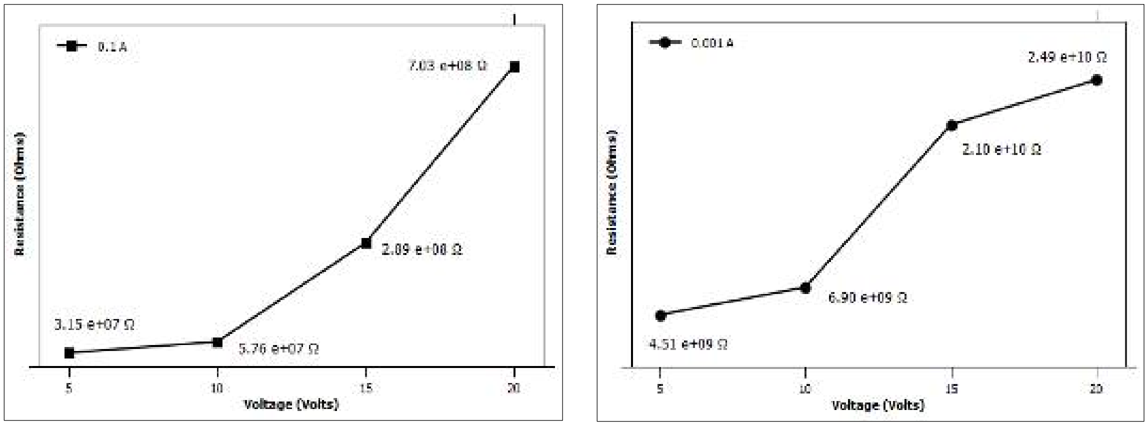

Fig.5. Resistances of the deposited PU thin films on glass substrate with 100% ESBO polyol replacement at different voltage limits at a constant current limit of 0.1 A (left) and 0.001 A (right).

3. CONCLUSION

Polyurethane thin films were successfully deposited on glass substrate utilizing 50% and 100% bio-based ESBO replacements as well as 100% petroleum-based polyols. We found out that the 100% ESBO replacement is comparable to the 100% petroleum-based polyols in terms of its uniformity and homogeneity of the deposited PU thin films. Optimum spinning speed is necessary to attain the desired thin film properties suitable for dielectric material application. Maintaining the stoichiometric ratio between O-H and N-C-O vibrational modes closer to unity is one of the most important factors in order to produce a high quality PU thin film. Higher thermal stability for the 100% ESBO replacement was observed.

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