Thermal and Chemical Stability of a Spin-Coated Epoxy Adhesive for the Fabrication of a Polymer Optical Waveguide

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Spin coating is a common method for depositing very thin polymeric film across a planar surface in a short period of time. Thinning occurs due to the combined effects of centrifugal spin-off and evaporation. The evaporation of any reactive component during spinning plays an important role on the stability of spin-coated polymeric film. An investigation was carried out to study the effects of spinning on the thermal and chemical stability of the epoxy adhesive. The thermal stability of both spin-coated and without spin-coated epoxy adhesive was measured by thermogravimetric analysis (TGA) at heating rate of 10 °C/min in an inert environment. A lower thermal stability was observed for the spin-coated epoxy adhesive. At the center of the substrate it is more stable than the other locations. Thermal stability greatly deviates at the border side of the spin-coated substrate. Higher chemical stability was also observed at the center than the other locations of the spin-coated layer when immersed in the metal (nickel) etchant chemical solution. The lower thermal and chemical stability is mainly due to changes in the material properties during the spinning process. From this study it is proposed to use the reactive components that are less volatile, having higher intermolecular forces, and allow a greater part of the thinning behavior to occur without significant changes in the fluid properties during the spinning process. Lower spin speed also suggested to reduce the mechanical degradation of the polymeric adhesive for the fabrication of a polymer optical waveguide.

1. Introduction

Epoxy resins have been used commercially in many industries due to their many attractive properties such as good mechanical behavior, electrooptic properties, adhesive strength, chemical resistance, ease of processing, and low cost. This has also lead to a wide range of adhesive applications in the manufacturing of various electronic and photonic structures, devices, and assemblies.[1] A typical polymeric adhesive as a cladding material is offering integratable photonic devices for the fabrication of polymer optical waveguides.[2] Figure 1 shows the overview of one of the photolithography processes for the fabrication of an inverted rib polymer optical waveguide using benzocyclobutane (BCB) as core and epoxy as cladding material. In this application, after the deposition of initial cladding layer, additional heating and chemical etching is required for the fabrication in the subsequent step of photonic devices. Therefore, the polymeric material should have sufficient thermal and chemical stability to withstand typical fabrication processing and operation condition with good performances.[3]

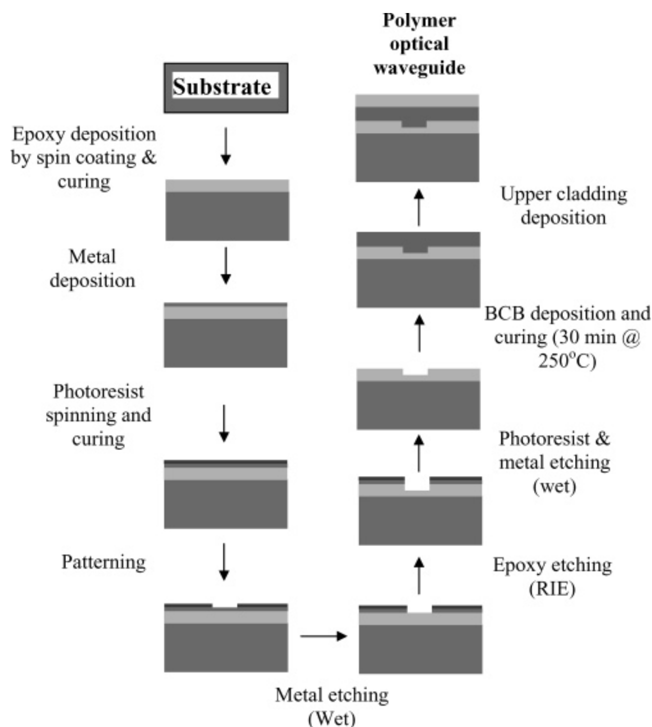

Figure 1. Overview of the photolithography process for the fabrication of a polymer optical waveguide.

The key requirements for a polymer optical waveguide include a simple and straightforward thin film deposi-

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tion process.[4] It can be deposited by a variety of techniques with different complexities and applicabilities. The choice of deposition technique depends on the physicochemical properties of the material, the film quality requirements, and the substrate being coated. The final properties of these films also depend on their morphologies that are largely affected by the polymer chain orientation and the state of aggregates. Typical polymeric solutions are complex mixtures of solvents, stabilizers, surfactants, and precursor molecules that have been designed to optimize various coatings characteristics.[5] Reactive solvents have an important role in the curing of polymeric adhesives. The advantage of using reactive solvents is that both the processing temperature and viscosity can be lowered with respect to the polymer to be processed. In addition, there is no need for solvent removal after processing: the solvent becomes a useful structural part of the final system, depending on the proper reactive solvent (monomer).[6]

One of the simplest and most common techniques of applying thin films onto wafers is spin coating. This technique is assumed to lead to a very uniform film with well-controlled thickness.[7] Due to the complexity of common spin-coating solutions, the behavior of mixed solutions should be understood under the conditions of rapid fluid flow and convectively driven evaporation that occur during the spinning. Many studies have been directed to predict final film thickness, but no attempt has been paid to the changes in thermal and chemical stability induced by the spinning process. The knowledge of stability, degradation, and mode of decomposition under the influence of heat and chemical solution is very important in the processing optimization. The threshold gives an indication of the ultimate processing condition that can be used during the subsequent fabrication and operation process. Proper understanding of potential degradation mechanisms can greatly aid the appropriate selection of material and process parameter in the fabrication and extend the outdoor longevity of the product.[8] The aims of this paper are to study and understand the effect of spinning on the thermal and chemical stability of epoxy adhesive. Thermogravimetric analysis (TGA) was used to explore the thermal stability of both spin-coated and without spin-coated epoxy adhesive. When the adhesive was chemically and physically changed, the TGA showed significant reduction in weight at that effective temperature. Chemical resistance was measured by the changes in refractive index and microscopic observation before and after immersion in metal−etchant−chemical solution. A better understanding of the effects of the spinning on the thermal and chemical stability is important in making high-quality polymer thin film. The results of this study can allow manufacturers to develop highly reliable and better performance polymer optical waveguides for photonic devices.

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Table 1. Curing Conditions for Different Sample Preparations

sample	curing conditions		remarks
	UV curing	heat curing	
A	2 min at 4000 mW/cm^2		without spin
B	2 min at 4000 mW/cm^2	10 min at 120 °C	without spin
C	10 min at 4000 mW/cm^2	10 min at 120 °C	spin coated

2. Experimental Section

2.1. Adhesive Material. The polymeric adhesive used in this study is an epoxy-based commercial UV-curable adhesive. It is a clear, slightly amber in appearance, and 100% reactive liquid that can be cured readily by exposing to UV light. The viscosity of this adhesive is less than 100 cps at 75 °F. It is consist of mainly (i) epoxy resin and (ii) a hardener. The term "epoxy" refers to a chemical group consisting of an oxygen atom bonded to two carbon atoms that are already bonded in some way. The simplest epoxy is a three-member ring structure known by the term "α-epoxy" or "1,2-epoxy". The hardener, often an amine, is used to cure the epoxy by an "addition reaction". During the curing, the epoxy resin reacts with amine and forms a complex three-dimensional molecular structure. The cured adhesive is also optically clear. The glass transition temperature (T_g) of the adhesive is 120 °C.

2.2. Sample Preparation. The substrate used in the experiments was a highly polished silicon wafer. Organic residues on the silicon-covered surfaces were removed by the successive ultrasonic cleaning with acetone, alcohol, and DI water. Throughout this investigation, 2 cm × 2 cm square edge silicon wafers were used to avoid the radial nonsymmetry in the rectangular substrate that causes larger corner buildup effects on the spin-coated polymer film.[9] All the samples were handled and processed in a class 100 clean room. Ambient temperature was constant at 20 °C, and relative humidity was maintained at 80%. The adhesive was removed from the refrigerator and allowed to warm to room temperature before processing. Samples of both without spin and with spin were prepared.

For without spin, small sample quantities were placed on cleaned silicon wafer. In case of spinning, the films were deposited with a precision spin coater in a glovebox. The deposition process involves the dispensing of fluid onto a stationary or slowly spinning substrate. An excessive amount of fluid is used to prevent coating discontinuities caused by the fluid front drying prior to it reaching the wafer edge. Spin speed and time were 3000 rpm and 30 s, respectively. The samples were then cured by using various curing conditions. The curing process of this adhesive consists of a rapid polymerization initiated by UV-reactive photoinitiators and postthermal exposure. Table 1 shows the curing condition for different prepared samples. The Kasper mask aligner with 350 W high-pressure mercury arc lamp was used for UV curing. The light guide opening of this mask aligner is 8 cm in diameter, and the sample was easily placed at the center of the light guide for uniform light exposure all over the sample. The heat curing was completed simply on a hot plate. To obtain the desired weight of spin-coated adhesive for thermogravimetric analysis, a greater thickness of multilayer depositions was required. It was necessary to deposit five subsequent spin-coated layers on the substrate to obtain the film thickness ranging from 15 to 20 μm. However, the cured adhesive shape of the without spin sample is just like the drop on the substrate and the dimension depends on the drop size. In this study the drop size was 2−3 mm in diameter and 0.5−1.0 mm in height, but only a part of the drop was used for thermogravimetric analysis.

2.3. Thermal Stability Measurement. Thermal stability refers to the sustainability of adhesive toward physical and chemical properties changes when it is exposed to high thermal loading. TGA was performed with a Seiko instrument (SII-

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TG/DTA 220). Very small amounts of cured adhesive (about 1 mg) were removed form the substrate and placed in an open aluminum sample pan. Dry helium gas was introduced into the test furnace as the test environment for an inert atmosphere. The experiments were performed at a 10 °C/min heating rate in the temperature range 30−600 °C. The apparatus consists of a microbalance within a furnace, allowing the weight of the sample to be continuously monitored while the temperature is controlled.[10] The change in sample weight during the thermal scan is calculated as follows:

$$\text{weightloss} = \frac{W_\text{i} - W_t}{W_\text{i}} \times 100\%$$

Here W_i is the initial weight before the TGA test and W_t is the weight at a certain temperature during the scan. A curve of weight loss versus temperature was then obtained.

2.4. Chemical Stability. Photolithography is one of the main processes for the fabrication of a polymer optical waveguide. As shown in Figure 1, the fabrication process needs metal deposition (a few hundred nanometers) on initially deposited polymer layer for masking. The common metal nickel has been used precisely as a hard mask, which exhibits a high durability in fluorine reactive ion etching (RIE) of polymer.[4] Once the pattern is developed, the metal needs to wet etch from the selected portion before RIE. After the RIE process the remaining nickel mask is stripped off by the same wet etching process. The commercial etchant normally used for this wet etching is a mixture of acid solutions (3:3:1:1 H_3PO_4−HNO_3−CH_3COOH−H_2O). Therefore, the polymeric materials also need to be chemically resistive in that solution.

Chemical stability of the cured adhesive can be determined by exposing standard samples to the chemical solution and recording changes in physical properties, before and after exposure by a standard test method. The tests were carried out at temperature of 70 °C for 20 min according to the procedure ASTM D 543-52T.[11] To measure the chemical resistance, samples B and C (prepared according to section 2.2) were completely immersed in the nickel etchant solution. The specimens were then removed from the solutions, rinsed immediately with deionized water, and dried on hot plate. After the acid-immersion tests, surface morphologies of the coating were examined in an optical microscope for their film appearance. The change in refractive index of the coated layer is also measured for different immersion times by using the prism coupler method.

3. Results

3.1. Thermal Stability. Thermogravimetric analysis (TGA) is a method used to measure the weight loss of material due to formation of volatile product.[10] Figure 2 shows a typical TG diagram (weight loss during the temperature rise) of cured epoxy adhesive (samples A and B) that was not spin coated. On the TG curves, the weight of the sample is initially almost stable at lower temperature. The onset temperature of the weight loss step is defined as the initial degradation temperature. At this temperature highly volatile components or moisture existed in the adhesives in a state of free or loosely bound water starting to evaporate.[12] Above the initial degradation temperature, the weight loss gradually increases due to the removal of strongly confined, bound, or chemically linked water at higher temperature.[13] Small molecules produced by the pyrolysis of the polymeric material also caused the greater weight loss or degradation in this temperature range.[14] The temperature at which the weight loss is about 10% is defined as degradation temperature. It is a good indicator of the thermal stability of the polymeric material. At higher temperature, most weight loss occurred in a short temperature range, where the line is steepest; the adhesive decomposed quickly to vaporized gaseous particles and a solid residue or ash depending upon the nature of the degradation pattern. This temperature is called the decomposition temperature.[15]

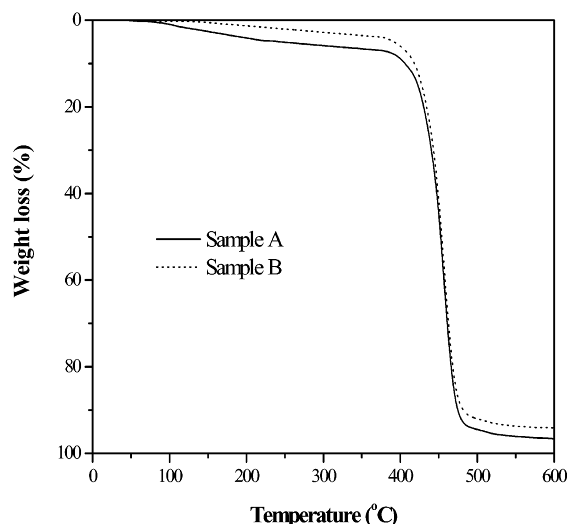

Figure 2. Thermogravimetric results of the epoxy adhesive that was not spin coated.

3.1.1. Effect of Postheat Exposure. The weight loss profiles for those two samples (samples A and B) are almost similar throughout the weight loss process and differ only at initial degradation temperature, at which sample B is more stable than sample A. Lower initial degradation temperature was observed for sample A (70 °C) than sample B (100 °C). Because sample A was not postcured by heat after UV curing, it may contain absorbed moisture if the adhesive existed in a state of free or loosely bound water that started to evaporate at low temperature. It also indicates that only UV light energy is not sufficient for optimum curing of UV-curable epoxy adhesive and needs postthermal exposure for moisture evaporation. The major concern involving the presence of moisture at elevated temperatures is hydrolytic degradation. It is a chemical change which occurs when moisture is present above or near the glass transition temperature (T_g) of the polymer. It causes random chain scissions to occur, which causes a reduction in molecular weight and, in turn, a reduction in mechanical integrity of cured adhesive. Another reason for the higher stability of sample B is the increased cross-linking density due to the postthermal exposure.[16] The anhydride group and hydroxyl group of the resin react to form ester cross-links. These ester networks are more thermostable than other types of linkage.[17]

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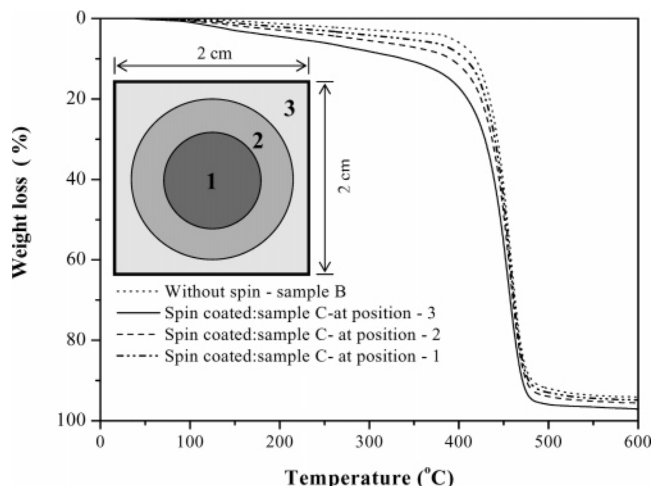

Figure 3. Effect of spin coating on the thermal stability of epoxy adhesive.

Table 2. Comparison of the Stability Changes Due to the Degradation of Epoxy Adhesives

		characteristic temp (°C)		
sample	posn	initial degradatn	degradatn	decomposn
A		70	408	448
B		100	416	450
C	1	90	407	445
	2	70	385	438
	3	55	338	432

3.1.2. Effect of Spinning. Thermal stability of spin-coated adhesive film (sample C, over 3 locations) was also measured using the same TGA method. Figure 3 shows the corresponding TG curves for three different locations (indicated in the inset of the figure) of sample C with that of sample B. A comparison of the stability change due to the spin-induced degradation of epoxy adhesive determined here with other previously found characteristic temperature is shown in Table 2. The result shows that the thermal stability decreased for spin-coated adhesive film compared to adhesive that was not spin coated. Thermal stability also varies at different locations of the spin-coated substrate. At the center of the substrate it is higher than the other locations. The lower thermal stability is mainly due to changes in material properties. The spin-coated liquid usually contains a volatile component that evaporates during spinning and leaves behind a thin solid film. Solvent evaporation from the film alters the material properties (e.g., viscosity, diffusivity, vapor pressure, surface tension). The higher degree of uniformity in the evaporation rate leads to a similar uniformity in the final polymer film properties.[18] But nonuniformity induces the degradation to various degrees at various locations of the spin-coated epoxy adhesive during the spinning process.

3.2. Chemical Stability. Chemical stability is determined by the material's ability to withstand changes from chemical contact. This issue involving corrosive fluid exposure should be evaluated to ensure a chemically stable polymeric thin film for the optical waveguide. The immersion test shows that the spin-coated epoxy surfaces were also deteriorated to various degrees at various locations of the spin-coated epoxy adhesive. Figure 4a shows the optical micrograph of sample B after the immersion in metal etchant. It is very clear that the without spin sample surface is chemically stable in that solution and there is almost no change in surface morphology. However for the spin-coated sample C, it shows some different results. Figure 4b−d displays the optical micrographs of different locations of the spin-coated cured adhesive after immersion in solution. The chemical attack leads to porosity in the polymer interface, which results in excessive increase of optical loss. The spinning also affects the refractive index of the cured adhesive. Figure 5 shows the refractive index of spin-coated adhesive before and after immersion in chemical solution. Before immersion higher refractive index at the corner and after immersion higher drop also indicate the lower stability at that portion.

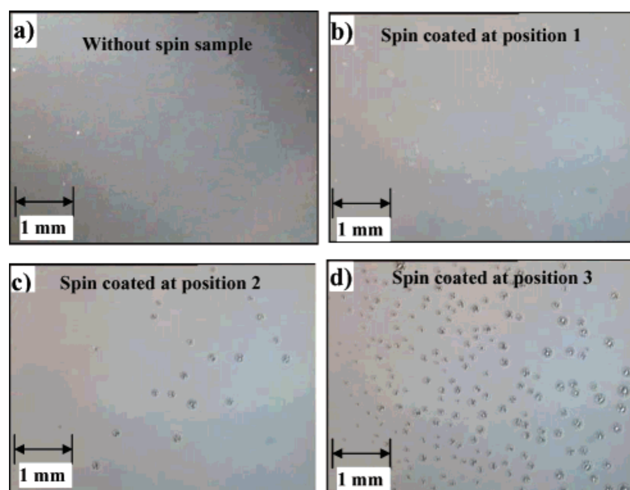

Figure 4. Optical micrograph of the cured epoxy after the immersion in metal etchant (a) without spin, (b) spin-coated position 1, (c) spin-coated position 2, and (d) spin-coated position 3.

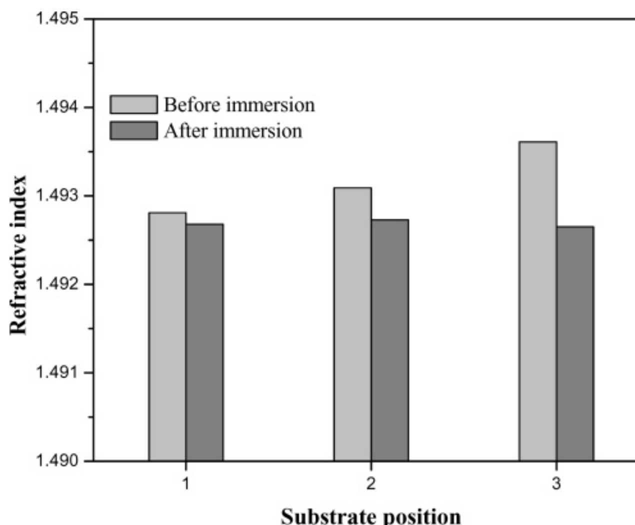

Figure 5. Refractive index of spin-coated cured adhesive before and after immersion in chemical solution.

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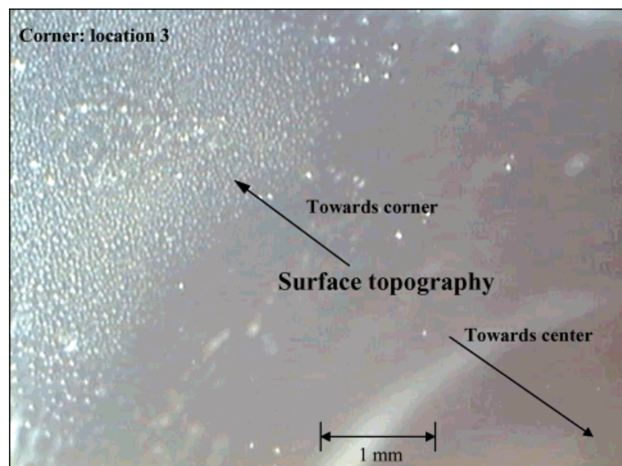

Figure 6. Surface topography near the corner of the spin-coated adhesive film.

4. Discussion

Earlier studies have found that the curing reaction rate of spin-coated epoxy adhesive is much slower than that of without spinning. The reaction rate at the center (location 1) is also higher than other location of the substrate. The slower reaction rate is mainly due to changing the material properties during spinning.[9] It clearly indicates the spin-induced degradation of spin-coated epoxy adhesive during the spinning. In comparison to the without spin-coating sample, the thermal and chemical stability of spin-coated adhesive decreased mainly due to the following:

4.1. Mechanical Degradation during Spinning. Under the influence of spinning forces, intermolecular interactions between certain molecules at certain sites of the polymer are disrupted. Spin-induced main chain rupture might also initiate the fragmentation of linear polymers.[19] This type of chain scission plays a significant role in the thermal and chemical stability of polymeric material.[20] During the heating or chemical etching, very little energy needs to be fragmentized and there is exhibited lower stability of spin-coated polymeric film.

4.2. Changes in the Ratio of Resin and Hardener. Epoxy resin is more volatile than the hardener (amine). Therefore, the evaporated amount of epoxy resin is larger than that of amine during the spinning. As a result, the correct mix ratio of amine and epoxy to ensure the complete reaction of that reactive component is disrupted. Since the amine molecules "coreact" with the epoxy molecules in a fixed ratio, unreacted amine remains within the matrix after the cure reaction, which alters and affects the final properties of the adhesive.

4.3. Void Formation. Due to the variation in spinning force and surface tension, the topography also varies at different locations of the spin-coated adhesive film. Figure 6 shows a micrograph of the surface topography at the corner of the spin-coated adhesive. The figure clearly shows how the topography differs from center to the corner due to the spinning process of the adhesive. As shown, there are a large number of voids at the corner and almost no voids at the center side of the substrate. The void formed during the spinning and curing of epoxy adhesive released from the spin-coated adhesive layer at the heating or etching step and induced the excessive weight loss or porosity.

4.4. Cross-Linking Density. Spinning can also induce a phase separation in the adhesive formulations, which have different cure rates.[9] Lower curing degree, higher mechanical degradation, and more void formation decrease the cross-link density. Figure 7 shows the schematic of different cross-linking densities before and after curing. Decreasing cross-link density, that is, increasing the distance between reactive sites, usually has the effect of reducing thermal and chemical resistance by decreasing the compressive and tensile modulus as well as the impact. Less thermal or chemical energy is required to degrade a given mass into its volatile products.[11]

At the periphery of the substrate, the polymer experienced highest spinning force, more void, and lower cross-link density. Therefore, the lowest thermal and chemical stability observed at the periphery of spin-coated adhesive is due to rapid fluid flow and convectively driven evaporation that occur during spin coating. On the other hand, at the center of the substrate, the highest stability observed is due to lowest stress, no void, and higher cross-link density.

5. Conclusions

The effect of spinning on the thermal and chemical stability of epoxy adhesive was studied. Lower stability was found for spin-coated adhesive compare to the adhesive that was not spin coated. This is mainly due to the changes in material properties during the spinning. A possible phase separation of the components of adhesive formulation and possible mechanical degradation of polymer chains due to stretching during the spinning process seem to alter the material property. Evaporation of reactive components during the spinning also disrupted the fixed ratio of epoxy and hardener. Therefore, the full conversion of those components also was not completed. As a whole, the spin-coated adhesive holds lower cross-linking density as well as lower thermal and chemical stability. Stability is lowest at the

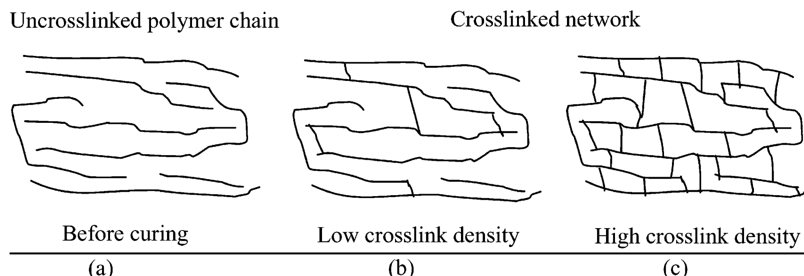

Figure 7. Schematic of different cross-linking densities before and after curing.

border side of the substrate. The problem associated with spinning results primarily from instability to thermal decomposition at elevated temperature and susceptibility to chemical attack by corrosive environment. The spin-induced degradation also leads to the loss of useful optical and mechanical properties. To overcome those problems, reactive components those are less volatile and having higher intermolecular forces should be used to reduce the evaporation and phase separation during the spinning. Slower spin speed should be also selected to minimize the mechanical degradation of the polymeric adhesive.

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