

Improvement of Adhesion and Reliability of Conductive Inks on Flexible Liquid Crystal Polymer Substrates

D. Muse, S. Pritchard, E. MacDonald, R. Wicker
W. M. Keck Center for 3D Innovation
The University of Texas at El Paso

X. Chen, M. Newton, K.H. Church
nScript, Inc.
3251 Progress Drive, Suite D
Orlando, FL 32826

Abstract

The emergence of printed electronics as an industry has been growing and recognized in application areas such as antennas, RFID, displays, and photovoltaic cells. Paramount to the success of these devices is reliable conductive inks that adhere to the substrate after successive bending and stretching and maintaining a constant resistance with time. Furthermore, for high performance electronics, new substrates will be required that allow RF performance deep into the GHz regime. This paper describes an evaluation of commercially available inks on Kapton® and Liquid Crystal Polymer (LCP). Kapton® is a well known substrate in printed electronics and previous reliability evaluations have shown inks are generally formulated to adhere well to this substrate. LCP is a relative new material in the electronics industry and this study shows that additional pre-processing of the substrate is necessary to obtain similar reliability and adhesion performance as compared to Kapton®.

Keywords: direct-printing, micro-dispensing, ink adhesion, Liquid Crystal Polymer

Introduction

A wide variety of new electronics applications are emerging as a result of advances in flexible electronics and will inevitably include intelligent clothing, active prostheses with unique fit, large foldable and inexpensive displays, RFID, and disposable circuits, to name a few. Progress in displays, organic transistors, antennae, and flexible batteries has been recently reported [1-7]. However, more effort is needed in understanding the performance and reliability of printable ink conductors and the corresponding relationship with the flexible substrates on which these inks reside.

Kapton® is a well known dielectric polyimide material that has a long history within the electronics industry and has adequate insulating and temperature characteristics. Alternatively, Liquid Crystalline Polymer (LCP) has been investigated since the early 90's and has recently been demonstrated with significant improvement in terms of the corresponding mechanical properties. For high frequency applications where low loss tangents and insertion delays rely on the material's high frequency characteristics like moisture content, dielectric loss and surface roughness, LCP has been shown to have strong potential. LCP is flexible and lightweight with exceptional electrical properties at higher frequencies [8-15]. Another advantage of LCP is the higher post

process temperature limits, which depending on the specific LCP material, can exceed 300°C.

In this paper, LCP is investigated as a candidate substrate for use with printed silver-based inks, which were originally formulated for use with more traditional flexible substrates such as Kapton®. Specifically, DC resistance and adhesion are tested on virgin LCP and Kapton® to understand the differences in reliability and performance. Subsequently, identical tests were completed on samples of LCP but only after the samples had been subjected to additional surface preparation, with the goal of improving the overall performance.

Methodology

In order to ascertain the reliability and performance of LCP with inks primarily targeted for use on Kapton®, DC resistance measurements were completed on samples of both substrates with four inks (Dupont 5064, Dupont CB028, CMI 125-15 and Parelec SPA201). Printing was completed with an nScript 3D 450 micro-dispensing system and the printed test structure included a serpentine line with a total of 7 bends and a total length of 2.5 feet on the underlying substrate, which was 5.0 inches long and 1.5 inches wide. All dimensions were taken from the IPC-TM-650 Test Methods Manual, Section 2.4.1E - commonly used for determining the adhesion and flexural capabilities of flexible electronic conductors.

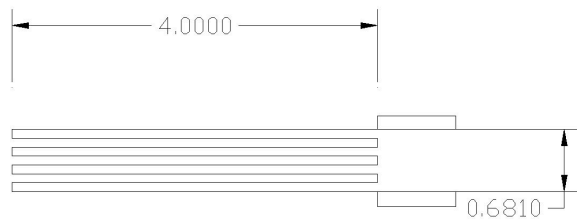


Fig. 1 – Printed Serpentine Structure

Furthermore, beyond printing on virgin LCP, two methods of surface preparation were included to evaluate potential methods of improving adhesion of inks to LCP – chemical and plasma pre-etching. The four inks that were initially identified for investigation were printed on Kapton® and virgin LCP, and subsequently, the most promising ink was also printed on both chemically-etched and plasma-etched LCP substrates.

The purpose of the proposed surface preparation was to increase the surface roughness of the LCP sample with the ambition of improving adhesion. Chemical etching was performed based on a recipe drawn from NAVSEA CRANE, Crane, IN. The process included treating LCP by immersing the substrates into a heated caustic solution consisting of concentrated aqueous potassium hydroxide (KOH) at 90°C for 2 to 3 minutes. This step is followed by a 5 minute acetic acid neutralization and distilled water rinse.

The plasma process was set up as an 85 minute time cycle with two time dwells. The first dwell focused on a gas mixture (CF₄, O₂, N₂) designed for surface etching to improve mechanical adhesion. The second dwell adjusted the plasma gas mixture (N₂, H₂) in order to change surface chemistries to improve ink wettability. All processing was done at 70°C. The specific initial times and gas mixtures were sourced to a process developed by March Industries and Rogers Corp. to promote adhesion on standard copper PCB plate. Since the results for printed inks were unknown, the process was run a second time leaving the overall cycle time the same, but increasing the etch part, and thus reducing the wettability to evaluate any change in the adhesion test results.

Results

The results of the original tests, including only Kapton® and virgin LCP, were presented at the Material Research Symposium in February of 2009. As expected in this initial evaluation, three of the four Kapton/ink combinations maintained the low resistances after an adhesion test had been performed as described in the ASTM D3359 standard (describing the application of tape to the ink sample and separating the tape in order to test the adherence of the ink to the substrate). However, all four LCP/ink

combinations become complete electrical opens after the same test was performed. Optical microscope images of samples at various stages of the test are shown for Kapton® and virgin LCP (Fig. 2 prior to the test, Fig. 3 after the test). Fig. 4 illustrates the removed ink on the tape after the test. One ink performed significantly better than the other four on the virgin LCP substrate (Dupont CB-028) as shown in the Figs. 3 and 4 and this ink was selected for evaluation with the surface-prepared LCP substrates.

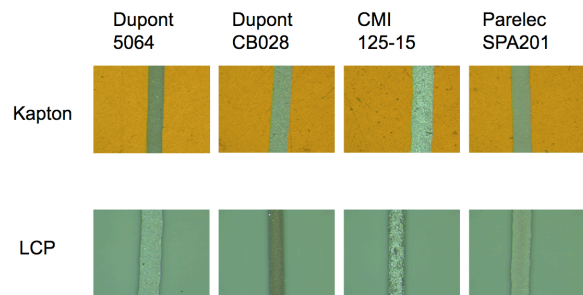


Figure 2 – Printed samples prior to adhesion test

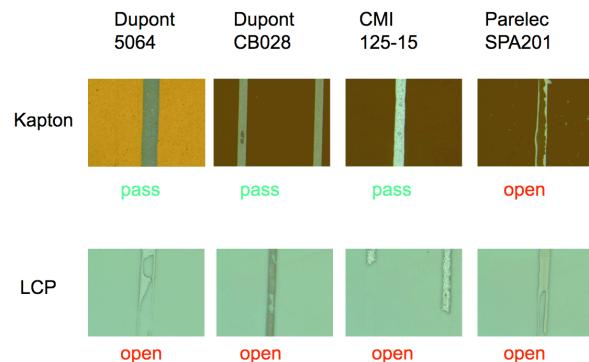


Figure 3 – Printed samples after adhesion test

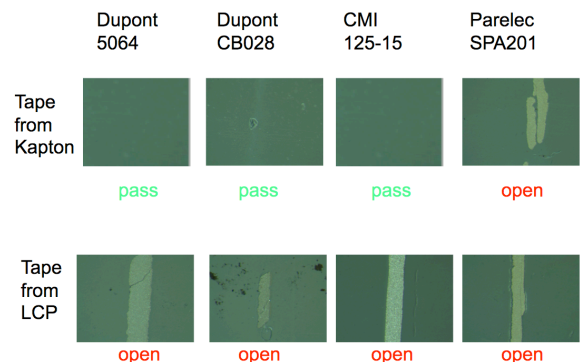


Figure 4 – Tape after adhesion test

The Dupont CB-028 ink was printed on four samples on four substrates: a) Kapton® as a baseline, b) LCP with the chemical etching, c) LCP with plasma etching Process 1, and d) LCP with plasma etching Process 2. The last three substrates were processed as described previously. Resistances were measured before and after the adhesion test, and average resistance values were calculated for each of the four substrates as shown in Table 1. All cases increased in resistance as the overall cross-section was decreased due to ink removal. However, in all cases, no visible ink was removed to the tape, which stands in stark contrast to the initial evaluation in which obvious signs of ink removal were evident – particularly for virgin LCP. Of the surface-prepared LCP samples, none performed as well as Kapton®, but even without process optimization, all cases were close to the performance of Kapton® and none resulted in open circuits as was the case with virgin LCP. Of the prepared LCP substrates, the plasma etching provided the closest performance to Kapton®, and the additional etching time provided a marginal improvement between Process 1 and Process 2. Further improvement in adhesion is expected with additional exploration of parameters of the plasma etch process.

Chemical etching – kinetically the most aggressive of the surface preparation processes - resulted in the highest resistance increases, but the process can likely be improved by evaluating chemical solution percentages and immersion duration. Additionally, one of the samples was an outlier and ignoring this data point pulls the chemical etching average in line with the plasma etching values. Furthermore, chemical etching is roll-to-roll friendly as opposed to

plasma etching, which requires a non-ambient environment with low pressure and high temperature.

Summary

The importance of LCP to the electronics industry for flexible applications will increase in the future given the substantial high frequency performance possible. Along with the on-going work to improve the LCP materials in terms of strength, moisture and temperature characteristics, this paper has described novel approaches to improve adhesion of printed conductors to this important substrate material. Further improvement is likely with additional evaluation of the process parameters. Future work is necessary to understand the implications on the RF performance, which may be degraded given the introduction of increased surface roughness necessary for the improved adhesion.

Acknowledgements

The facilities within the W.M. Keck Center for 3D Innovation (Keck Center) used here contain equipment purchased through Grant Number 11804 from the W.M. Keck Foundation, a faculty STARS Award from the University of Texas System, and two equipment grants from Sandia National Laboratories. This material is based in part upon work supported through the United States Air Force under Contract No. FA9453-08-M-0022 to nScript, Inc., the Mr. and Mrs. MacIntosh Murchison Chair I in Engineering, research contract N000140710633, the Office of Naval Research, and a research contract from the U.S. Army Space and Missile Defense Command and the Homeland Protection Institute to the UTEP Center for Defense Systems Research. The findings

Table 1 Process Comparison

Sample Number	S/N	Substrate	Initial Resistance (ohms)	Post Adhesion Resistance (ohms)	Percent Change	Process Average Percent Change
1	CB-028-01K	Kapton	14.2	14.5	2.1%	3.3%
2	CB-028-02K	Kapton	5.1	5.3	3.9%	
3	CB-028-03K	Kapton	5.5	5.7	3.6%	
4	CB-028-04K	Kapton	5.7	5.9	3.5%	
1	CB-028-01LC	LCP-Chem Etch	5.7	6.0	5.3%	7.5%
2	CB-028-02LC	LCP-Chem Etch	3.7	4.0	8.1%	
3	CB-028-03LC	LCP-Chem Etch	4.1	4.4	7.3%	
4	CB-028-04LC	LCP-Chem Etch	4.3	4.7	9.3%	
1	CB-028-R1-01LP	LCP-Plasma Etch (process 1)	7.4	7.8	5.4%	5.6%
2	CB-028-R1-02LP	LCP-Plasma Etch (process 1)	8.0	8.4	5.0%	
3	CB-028-R1-03LP	LCP-Plasma Etch (process 1)	6.8	7.3	7.4%	
4	CB-028-R1-04LP	LCP-Plasma Etch (process 1)	10.5	11.0	4.8%	
1	CB-028-R2-01LP	LCP-Plasma Etch (process 2)	8.8	9.1	3.4%	5.3%
2	CB-028-R2-02LP	LCP-Plasma Etch (process 2)	6.2	6.5	4.8%	
3	CB-028-R2-03LP	LCP-Plasma Etch (process 2)	4.8	5.2	8.3%	
4	CB-028-R2-04LP	LCP-Plasma Etch (process 2)	4.5	4.7	4.4%	

and opinions presented in this paper are those of the authors and do not necessarily reflect those of the sponsors of this research.

We would also like to extend appreciation with Tim Davis of JDM Associates and Lou Fierro of March Industries in assisting with the Plasma processing of the LCP substrate materials. Also, Dale Doyle of Rogers, Corp. on initial guidance in our quest.

References

- Holland, B.; Mcpherson, R.; Tan Zhang; Zhenwei Hou; Dean, R.; Johnson, R.W.; Del Castillo, L.; Moussessian, A.; "Ultra-thin, flexible electronics," *Electronic Components and Technology Conference*, May 2008, pp. 1110 – 1116.
- Nathan, A.; Chalamala, B.R., "Special Issue on Flexible Electronics Technology, Part I: Systems and Applications," *Proceedings of the IEEE*, Vol. 93, No. 7, pp. 1235 – 1238, July 2007.
- Nathan, A.; Chalamala, B.R., "Special Issue on Flexible Electronics Technology, Part II Materials and Devices," *Proceedings of the IEEE*, Vol 93, No. 8, Aug. 2005, pp. 1391 – 1393.
- Misra, V., "Emerging technologies in flexible electronics," *Electron Devices Meeting*, pp. 437 – 437, 2005.
- Sazonov, A.; Striakhilev, D.; Lee, C.-H.; Nathan, "Low-Temperature Materials and Thin Film Transistors for Flexible Electronics," *Proceedings of the IEEE*, Vol. 93, Issue 8, Aug. 2005, pp. 1420 – 1428.
- C.K. Liu, Tiu, P.K., D.C.C. Lam, "Rigid-flex electronics with printed passives," *Advanced Packaging Materials: Processes*, pp. 22 – 22, 2006.
- Junho Y., Sang-Gook M., Jae-Young J., "Design of antennas for a battery-assisted RFID tag with a thin and flexible film battery," *Antennas and Propagation International Symposium*, pp. 5463-5466, 2007.
- Vyas, R.; Rida, A.; Bhattacharya, S.; Tentzeris, M.M. "Liquid Crystal Polymer (LCP): The ultimate solution for low cost RF flexible electronics and antennas," *IEEE Antennas and Propagation International Symposium*, pp. 1729 – 1732, June 2007.
- Hao, Z.-C.; Hong, J.-S., "Ultra Wideband Bandpass Filter Using Embedded Stepped Impedance Resonators on Multilayer Liquid Crystal Polymer Substrate," *Microwave and Wireless Components Letters*, IEEE. Vol. 18, No. 9, Sept. 2008, pp. 581 – 583.
- Kingsley, N., Bhattacharya, S.K., Papapolymerou, J., "Moisture Lifetime Testing of RF MEMS Switches Packaged in Liquid Crystal Polymer," *Components and Packaging Technologies*, Vol. 31, No. 2, pp 345-3450, 2008.
- Thompson, D.C., Tantot, O.; Jallageas, H., Ponchak, G.E., Tentzeris, M.M., Papapolymerou, J., "Characterization of liquid crystal polymer (LCP) material and transmission lines on LCP substrates from 30 to 110 GHz," *Microwave Theory and Techniques*, Vol. 52, No. 4, pp. 1343-1352, 2004.
- Lu, Y. L., Huang, Y. P., Teo, K. C., Sankara, N. M.; Lee, W. L., Pan, B. H., "Characterization of dielectric constants and dissipation factors of liquid crystal polymer in 60–80 GHz band," *Antennas and Propagation Society International Symposium*, pp. 1 – 4, 2008.
- Ghiu, C.-D., Dalmia, S., Vickers, J., Carastro, L., Czakon, W., Sundaram, V., White, G., "Advanced 3D Packaging using Novel Liquid Crystalline Polymer Based Substrates," *Microwave Conference*, pp. 1771-1773, 2006.
- Farrell, B.; St Lawrence, M., "The processing of liquid crystalline polymer printed circuits," *Electronic Components and Technology Conference*, pp. 667-671, 2002.
- Altunyurt, N., Swaminathan, M., Sundaram, V., White, G., "Conformal Antennas on Liquid Crystalline Polymer Substrates for Consumer Applications," *Microwave Conference*, pp. 1-4, 2007.