Development of Hybrid Conductive Film with Primer

Nizamidin Jappar; Takeshi Hasegawa.
Kimoto Tech Inc.
Cedartown, Georgia USA
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Abstract

The ideal transparent electrode; conductive polymer coated film, and conductive silver nano-particle coated film, for flexible displays has been produced at lower cost, lower resistivity, higher transmittance and with improved flexibility property at the KTI (Kimoto Tech Inc) by using roll-to-roll process. Furthermore, KTI has developed a hybrid conductive film by using a simple and effective method, and achieved a highly conductive AgNP's (silver nano-particle) / conductive polymer composite mesh with excellent optical transparency and mechanical properties. This is achieved via applying PEDOT:PSS solutions sequentially to treat AgNP's films, resulting in AgNP / PEDOT:PSS composites. Thin films coated from this composite possess excellent mechanical, electric and optical properties.

The strong adhesion between AgNPs and the substrate is critical to obtain stable and robust AgNP films for wide application. The coated film's network, transparence, and conductivity were increased when polyethylene oxide functional acrylic monomers were used as primer which bound AgNP and substrate.

Kimoto's coating technology improves flexible conductive films by supplementing with consistent high electric conductivity, high transparency, excellent abrasion resistance, and weather ability. KTI adds value and functionality by applying a variety of proprietary coatings to plastic substrates on one or both sides.

Introduction

The transformation of rigid, glass based display concepts to flexible, lightweight, and bendable structures requires innovation not only in the development of new materials, but also in substrate handling and process technologies. The market direction for making flexible lightweight display requires developing new materials and changing glass to substrate, silica to carbon, ITO to flexible electrode. One of the challenges facing developers of flexible-display technology is the need for low-cost durable transparent electrodes. ITO has been the transparent conductor of choice due to its optoelectronic performance and lack of alternatives, but ITO exhibits certain drawbacks: brittle, costly to manufacturing, expensive, and limited supply of indium has raised concerns as to the long-term future of ITO, and there is an urgent need for novel transparent conductive electrode. There are several candidates, for example, silver nanowire (AgNW) [1-3], carbon nanotube [4], graphene [5-8], metal mesh [9], conductive polymer (PEDOT PSS) [10-13], and self assemble silver nanoparticle [14-16]. Compared with commercial ITO substrates, these candidates make compromises between optical transparency and electric conductivity.

For the large-scale fabrication and wide applications of these alternated materials to the ITO, there are several issues that need to be addressed. First, strong adhesion between AgNW, AgNP, PEDOT PSS and substrate is critical to obtain stable and robust conductive film for wide application. Second, effective connections between AgNWs or AgNPs are key parameter to achieve high conductivity and transparency [2].

Materials that combine electronic conductivity with optical clarity are sought for the fabrication of flat panel displays and other electronic devices. PEDOT:PSS has excellent transparency in the visible region, good electrical conductivity, and environmental stability. Unfortunately PEDOT:PSS, like most conducting polymers, is infusible and insoluble and therefore difficult to process in a thin-film form or in any other shapes. Lack of process ability has been a major impediment to the commercial acceptance of this polymer. Transparent conductive polymer coatings can be applied as thin coating (100-300nm) by conventional wet-coating methods. These include spray-coating, gravure, dip, spin, screen-print, and slot-die. Kimoto Tech Inc. (KTI) has developed a roll-to-roll coating methods using PEDOT:PSS type as a conductive polymer [12-13]. CP coatings have been fabricated on 2, 5, and 7 mm PET with conductivity 200 Ω/sq, 400 Ω/sq, and 600 Ω/sq respectively.

The paper consists of two parts: in the first part we present a developing of primer for silver nanoparticle coating, roll to roll coating process of AgNP, and characterization of structure, electrical, optical, morphological properties of coated materials; in second part, we present optical, physical, and electrical properties of hybrid AgNP with PEDOT PSS film.

Experiment and roll to roll process

1. UV curable primer

UV curable primer formulation was including oligomers and monomers from Sartomer (Urethane acrylic oligomer, Amine, hydroxyl, carboxylic acid, and ethylene oxide functional acrylic monomers were tested as a main ingredient of primer), photo initiators from Ciba chemical, and pigment from EVONIK industry (nano size silica oxide).

UV Curing condition: F600S, 600 watt/inch from Fusion was used.

2. Silver nanoparticle coating

Silver nanoparticle coating solution was obtained from Cima Nano technology, developed the proprietary SANTE® Technology, a silver nanoparticle technology that self-assembles into a random mesh-like network when coated on a substrate, enabling transparent conductors with excellent electrical conductivity, high transparency and flexibility.

3. Coating process

Kimoto Tech Inc. (KTI) has developed a roll-to-roll coating methods using AgNPs and PEDOT:PSS (CP) type as conductive materials. AgNP and CP coatings have been fabricated on 2, 5, and 7 mm PET. Transparent conductive films have been made on the KTI production line shown in Figure 1.

4. Characterization

Viscosity of coating solution was measured by The Brookfield DV-E; Transmittance, Haze was measured by BYK Haze-Gard Plus; Surface resistivity was measured using the four-point probe method with surface resistivity meter (Guardian manufacturing model SRM-232); Adhesion test, 1 inch of Nichiban tape was applied to Ag film surface and this tape was pull off very quickly; Surface scratch resistance was measured by applying 1000 g of weight on the Lens coating hardness test KIT (tip of KIT was wrapped by piece of cloth), put this weight on the coated surface, and move this weight gently; Surface and cross section photographs of AgNP coated film were taken on SEM, S-3000N (Hitachi High-Technologies Corporation), Note: The angle of a photograph is 60 degrees; Quantitative analysis was conducted by EDX (E-MAX300, HORIBA,Ltd.); Surface of Ag conductive line was evaluated by using Scanning Probe Microscope, SPM, NanoNaviReal Probe Station （Probe : DF20P2, Hitachi High-Technologies）

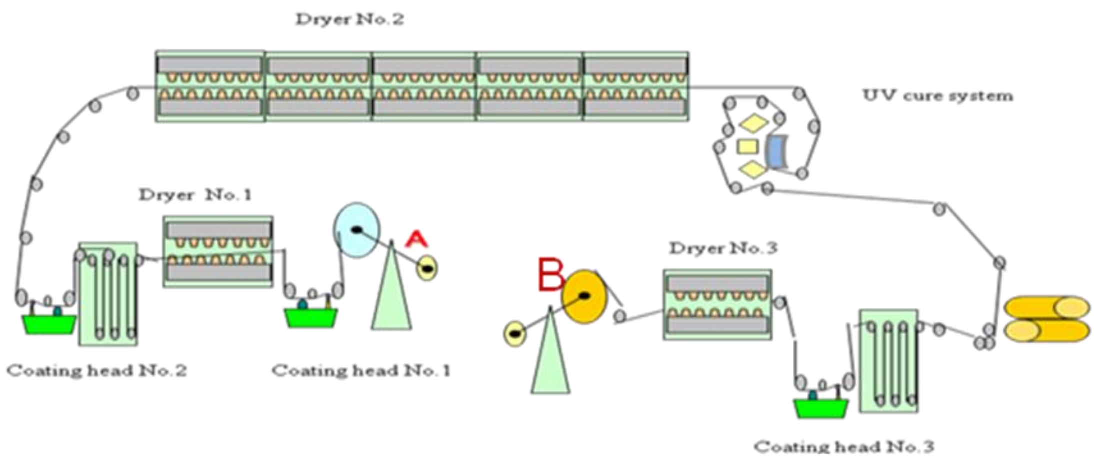


Figure 1: Kimoto Tech Inc.' Production Line

5. Hybrid conductive coating

Conductive polymer was coated by Mayer rod on the small –area (11x8.5 inches) of Ag NPs coated film. The dispersion of AgNPs was sonicated for 90 seconds and well agitated before do hand coating. The Ag NPs coated film was dried at 60ºC for 60 seconds, and conductive polymer coated film was dried at 130ºC for 60 seconds.

Results and discussion

1. Primer for AgNP coating

For the large-scale fabrication of AgNPs, there is an issue that needs to be addressed. The strong adhesion between AgNPs and the substrate is critical to obtain stable and robust AgNPs films for wide application. Silver nano particle solution is an emulsion, and it is difficult to get a good adhesion on the PET film while creating a good network structure due to the fact that the AgNPs dispersion solution has higher surface energy than the PET film. A primer layer is needed to create AgNPs conductive layer on the PET film.

Amine, hydroxyl, carboxylic acid, and ethylene oxide functional acrylic oligomers and monomers were tested as a main ingredient of UV curable primer's formulation. The coated film's network, transparency, and conductivity were increased in the order below: Amine < hydroxyl < carboxylic acid < ethylene oxide shown on the Figure 2.

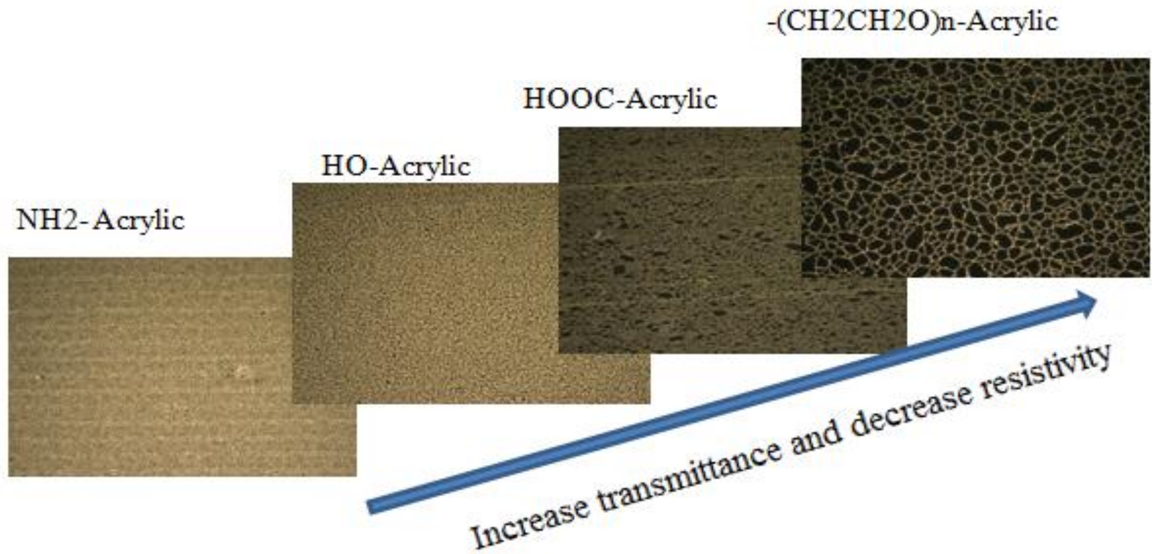


Figure 2. Primer functionality and AgNP network

Kamya at al [17] reported that polyethylene glycol (PEG) was appropriate as a stabilizer and polymeric media for reducing the $AgNO_3$ using β-D-glucose as s green reducing agent. The schematic illustration of synthesis of AgNPs capped with PEG is depicted in Figure 3.

As shown using the hydroxyl group of PEG as a capping agent can cover in the surface of AgNPs. They described that colloidal stabilization for [Ag(PEG)] occur due to the presence of Van der Waals forces between the oxygen negatively charged groups present in the molecular structure of the PEG, and the positively charged groups that surround the surface of inert AgNP.

We assume that UV cured polyethylene oxide acrylic polymer provided stronger crosslinking force between the PEG and polyethylene oxide acrylate polymer. Therefore, AgNPs capped with PEG were broke up from colloidal [Ag(PEG)], and AgNPs became agglomerated random network of conductive lines. The crosslinking force became weaker, and assembled AgNPs network line disappeared as an order of ethylene oxide > carboxylic acid > hydroxyl > Amine acrylate polymer. The effect of molecular structure of polyethylene oxide acrylate polymer to transparency of coated film was analyzed, and result is shown in Figure 4.

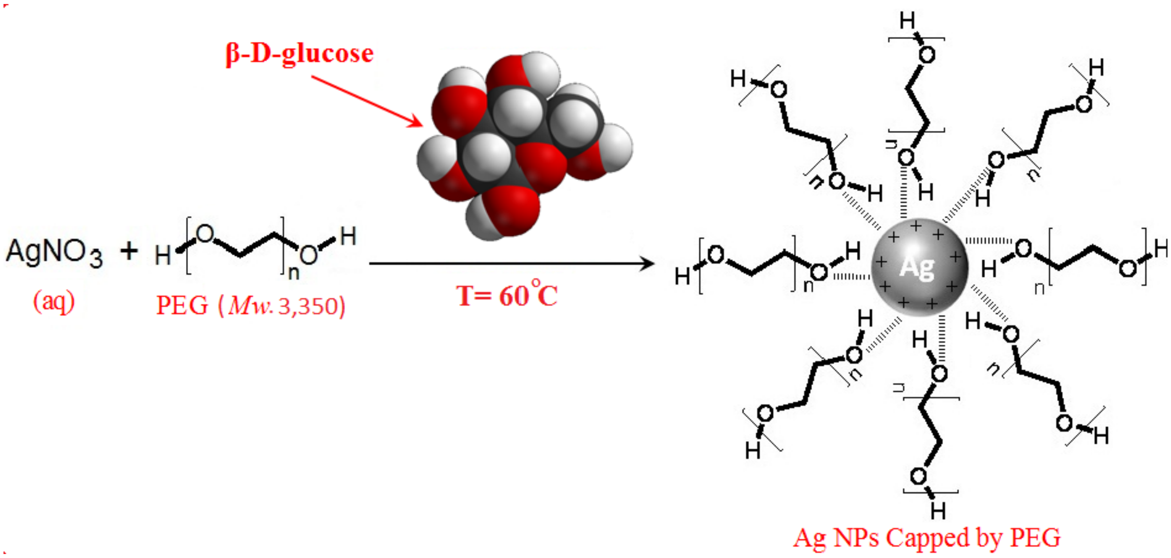


Figure 3. Schematic illustration showing the interactions between the hydroxyl groups in polyethylene glycol (PEG) present with the surface of positive charge of silver nonaparticles (AgPEG)

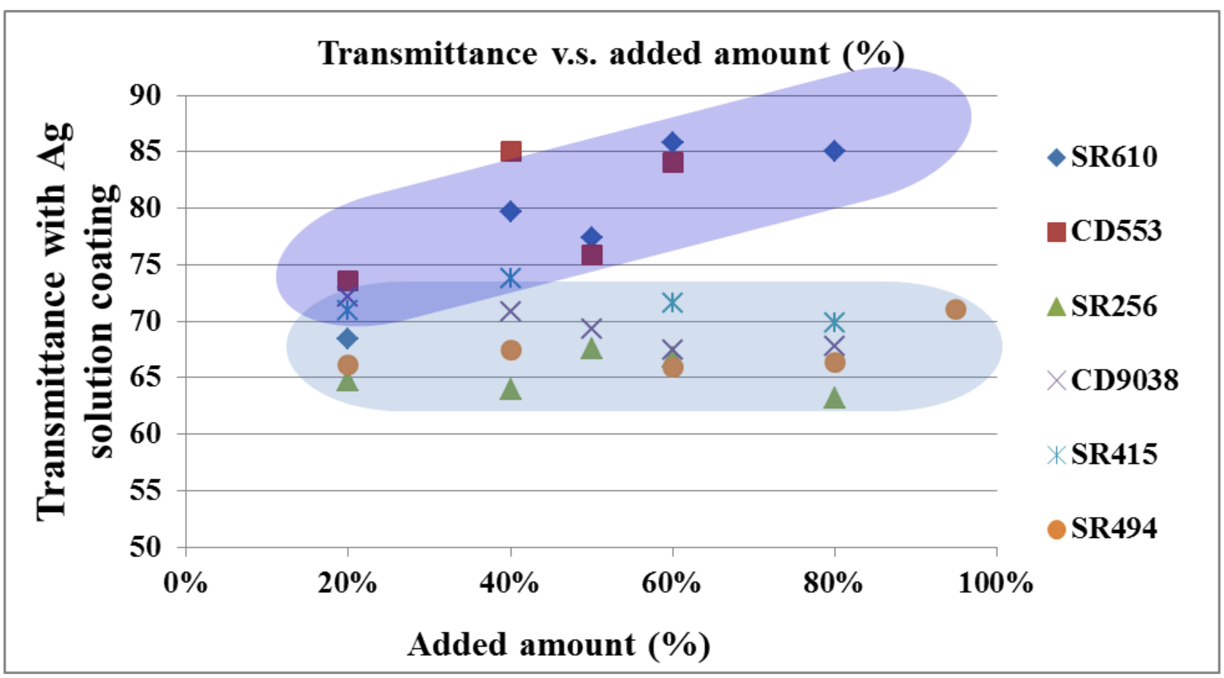
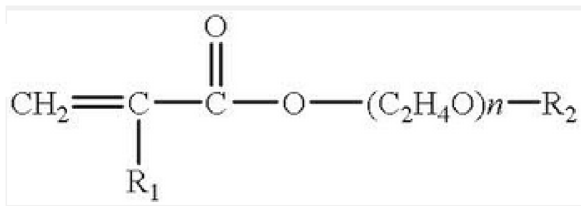


Figure 4. Transmittance of AgNP coated film verses molecular structure of polyethylene oxide acrylate

The transmittance of AgNPs coated film was higher than 80% when ethylene oxide number (-CH2CH2-O-)$_n$ in the polyethylene oxide acrylate molecular was higher than 12 and amount of poly ethylene glycol acrylate in primer formulation was higher than 60 percentage. The higher density of ethylene oxide group (-CH2CH2-O-)$_n$ provide higher bonding force to the polyethylene glycol (PEG), and results bigger pore size of AgNPs network.



2. Silver nanoparticle coating solution and circulation system

Viscosity of the AgNP solution is the key to get even and higher transparence conductive layer. Lower viscosity of coating solution and higher transmission of the coating was achieved when the sonication treatment time was higher than 90 seconds. The circle marked area is standard condition (three times of 30 sec treatment) as showing in Figure 5.

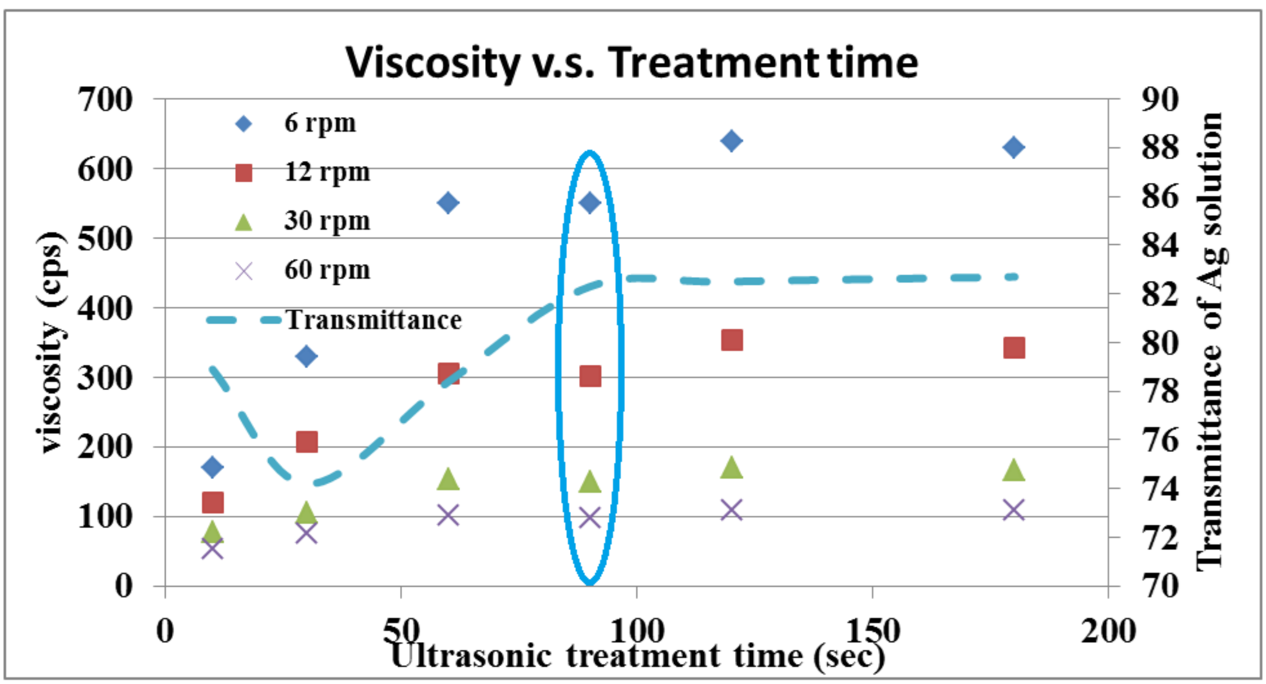


Figure 5. Sonicator treatment time verses viscosity of the solution, and transmittance of AgNPs coated film

One of the most important factors to fabricate large scale of AgNPs coating is how to adjust coating circulation system. AgNPs solution is emulsion system, and main challenge for coating is some type of defects such as air bubbles and ribbing, unevenness, etc. we designed a specific circulation system and coating head showing in Figure 6 to eliminate these issues. The across web even coating AgNPs conductive layer was achieved by using degassing unit along with a double pump system.

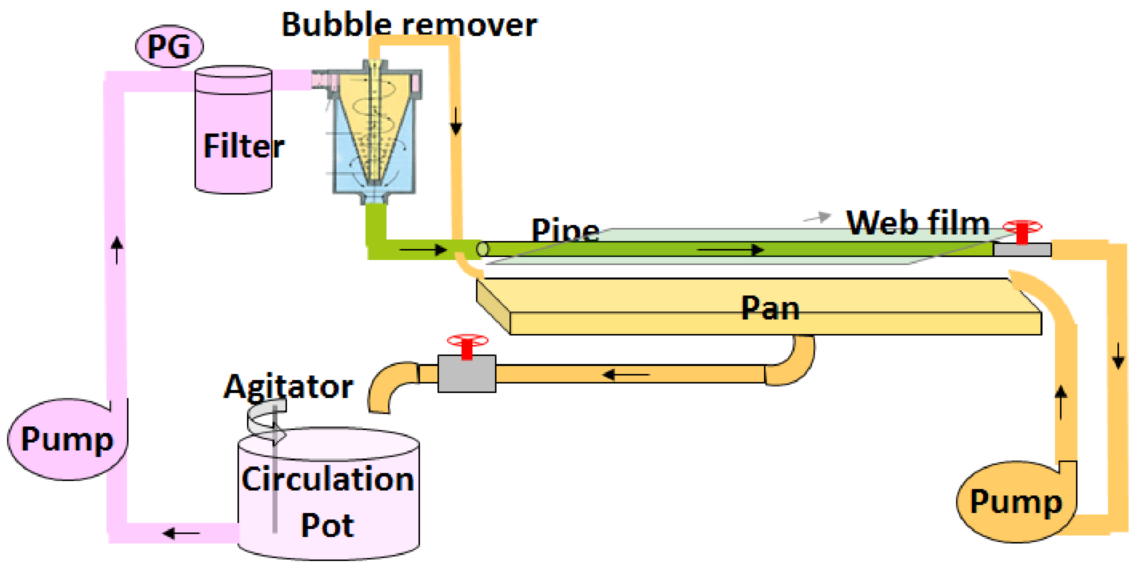


Figure 6. Large scale coating circulation system

3. Characterization of coated AgNP coated film

3.1 Characteristics of AgNP solution

Characteristic of AgNPs solution is self-aligns into a highly conductive transparent mesh within 30 seconds of being coated on a polyethylene oxide acrylate primer coated substrate; the microscope image is shown in Figure 7.

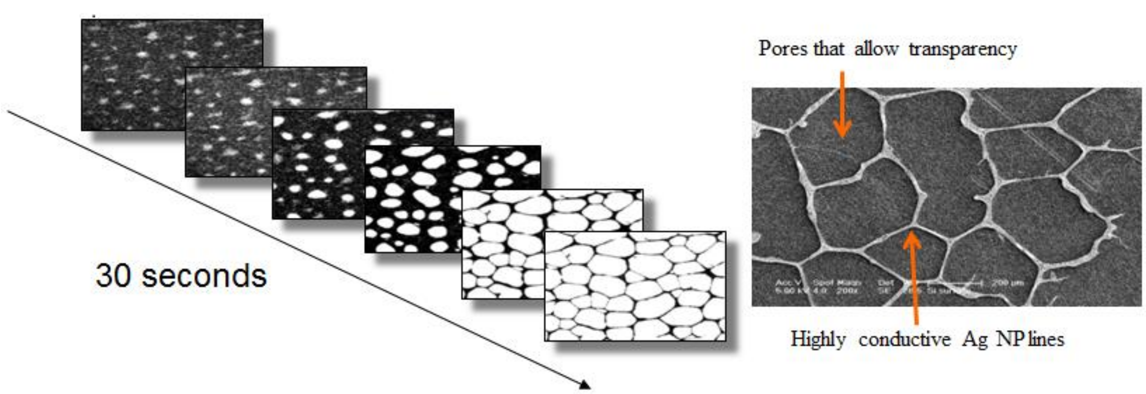


Figure 7. Microscope image of AgNP coated materials

Pore area of network allows transparency, AgNP lines are highly conductive. The connection between the AgNPs is mainly driven by capillary force from solvent evaporation, gravity, Van der Waals forces between AgNPs, and cross linking forces between the PEG and poly ethylene oxide acrylate of primer layer.

3.2 SEM

AgNPs conductive film morphology and thickness were evaluated by the scanning electron microscopy. The cross-section photograph of AgNPs film shown in the Figure 8 indicates the polycrystalline Ag nano particles, and line thickness is between 2-4 micron thick and 3-10 micron in width. The observed particle size in the original solution is 6-60 nm, while the particle distribution and capillary force seen during solvent evaporation cause variance of conductive line in size.

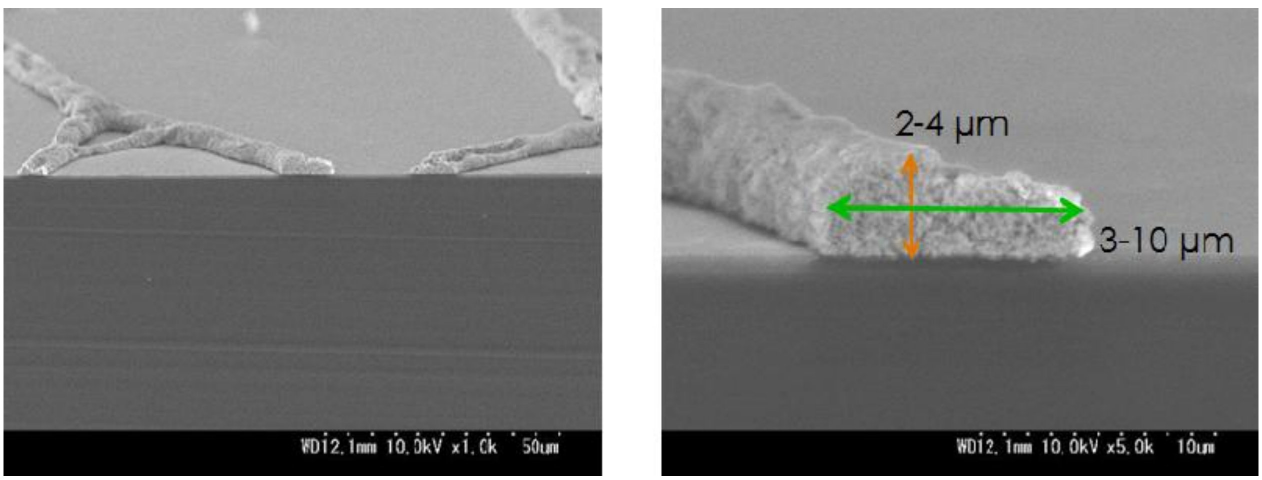
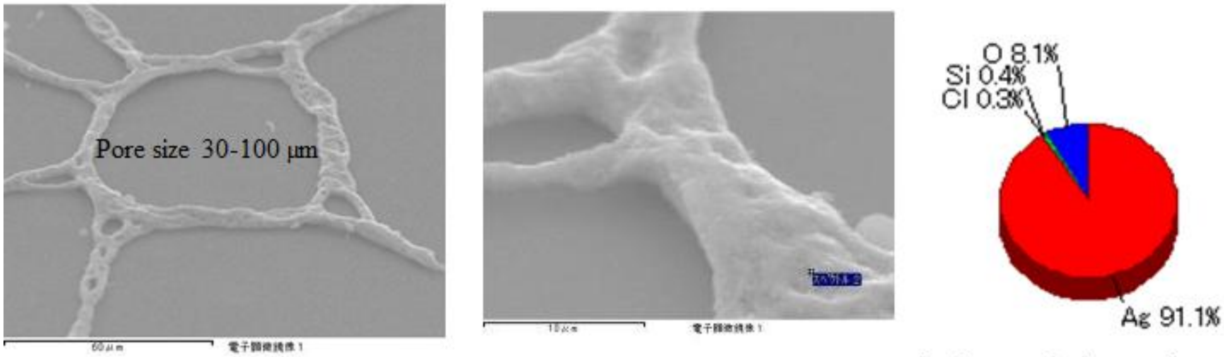


Figure 8. SEM Cross-section AgNP conductive film Image

3.3 SEM EDX

Mesh size and composition of AgNP conductive film was evaluated by SEM and Energy Dispersive X-ray, EDX. Mesh size is 30-150 microne, and the conductive AgNPs line is composed 91% of Ag, 8.1% of O2, 0.4 % of Si, 0.3 % of Cl (Note: Since the pretreatment of carbon vapor deposition is carried out for the EDX analysis, carbon was excluded). The coated materials become random mashes 30 seconds after coating due to the inter reaction between the AgNPs which is Cima Technology's proprietary emulsion formulation and specific primer layer. Even though the mesh size is random, it is narrow enough to make the coating transparent, and connect the mesh to each other to maintain a good conductivity path from edge to edge.

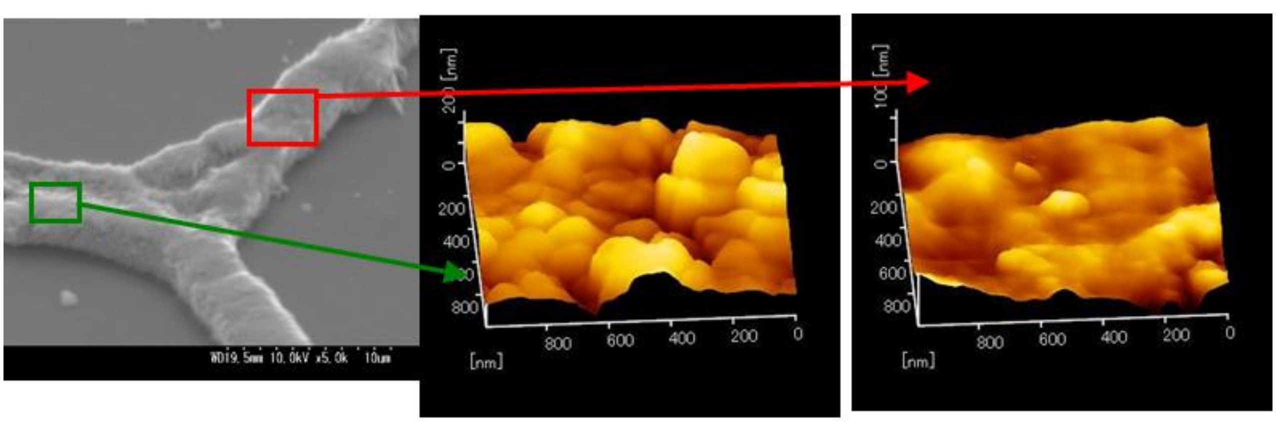


Mapping analyze Point analyze Quantitative analytic result

Figure 9. EDX Analysis of The AgNPs coating film

3.4 Scanning Probe Microscope, SPM

The surface of AgNP conductive line was evaluated by using Scanning Probe Microscope (SPM). Even though the measured points by SPM are actually different points from that of the SEM image, it is considered that; SPM image 1 is showing smooth part of the SEM image, and size is 5-60 nm, SPM image 2 is showing uneven part of the SEM image, and the size is 14-180nm. The elongated spherical morphology and agglomerates shapes, and the size deviation were observed. The conductive AgNPs line occurs extremely rapidly when curing process started, giving rise to small particle agglomeration (5-60 nm) which grow in a second stage to achieve higher size (14-180 nm).



SPM Image 2 SPM Image 1

Figure 10. SPM Observation of the AgNP Film

3.5 Cross web coating property

The transmittance and resistivity of AgNPs coated film on production line is shown in Figure 11. The transmittance is higher than 80 when the resistivity is about 10 ohm per square. Kimoto Tech (KTI) has developed a roll-to-roll coating methods using AgNP type as a conductive material. A uniform coating layer was observed cross the web by adjusting coating process, tolerance is in 3 %.

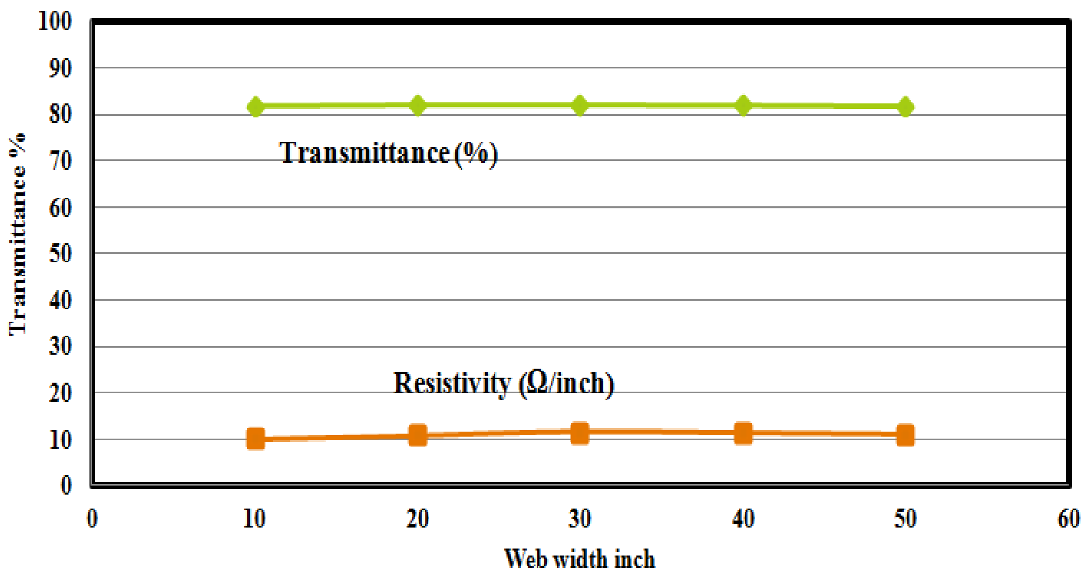


Figure 11. Transmittance and resistivity of AgNPs coated materials

4. Hybrid coating

4.1 Resistivity and optical properties of hybrid film

KTI has fabricated conductive polymer film and AgNPs film, achieving a high transparent, low resistivity, flexible, and low cost of conductive film by using KTI's proprietary roll to roll process. For these large-scale fabrication and wide application of AgNPs and metal mesh films, there are several issues that need to be addressed. First, effective connections between wires and meshes are the key parameter to achieve high conductivity and transparency. However, due to the polymeric compound on the surface of AgNPs and the loose contact between wire and mesh, extra treatments are often required to fuse the crossed wires or meshes together. Second, strong adhesion between AgNPs and the substrate is critical to obtain stable and robust conductive films for wide application. Substrate surface modification has been used to improve the adhesion of AgNPs on substrates by using primer coating.

The conductive polymer solution was coated on the Ag nano-particle conductive layer. The conductivity of hybrid film is increased 20 % at the retaining the haze level, the film transmittance is slightly decreased at 550 nm, due to the weak absorption of PEDOT:PSS in the visible range. The result is shown in Figure 12. The resistivity is slightly decreased and transmittance is decreasing when the amount of conductive polymer was increased. The contribution of conductive polymer to the conductivity of hybrid conductive film was lower than that of AgNPs due to the original conductivity of AgNPs is much higher than conductive polymer, PEDOT:PSS. After coating conductive polymer on the AgNPs coated film, the conductive polymer composite forms a thin and continuous coating on the AgNPs. It is clear that all the intersection point of AgNPs line and gaps between the AgNPs line are further covered by PEDOT:PSS polymer film. PEDOT:PSS coating acts as the connector on the AgNPs line and provides stronger binding forces through the entire AgNPs networks. With this result, we can understand the higher conductivity of hybrid film.

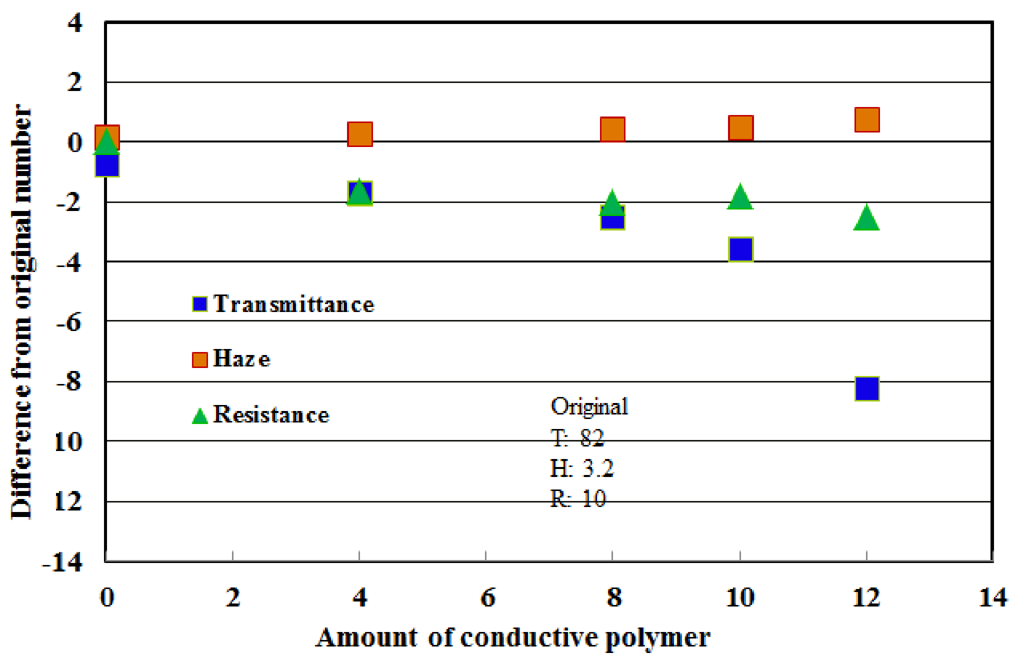


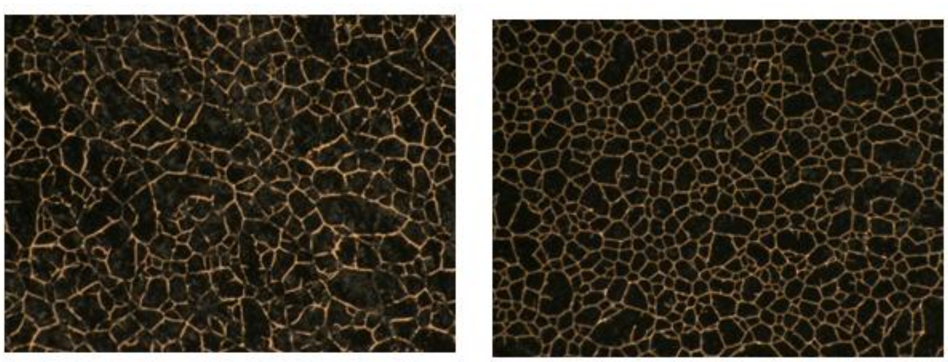
Figure 12. Optical properties and resistivity of hybrid film

4.2 Improve adhesive property

1 inch of Nichiban tape was applied to AgNPs film and hybrid film surface and was pulled off very quickly. The resistivity was measured in same place before and after tape was removed. The results are shown in the Table 1, and the microscope images are shown in the Figure 13. The resistivity of AgNPs film is increased from 10 ohm/sq to 26 ohm/sq after one time tape adhesion test, and the resistivity became unlimited after three times tape adhesion test. The connected AgNPs line was broken and pulled off after the one time type adhesion test as shown in the Figure 13. However, the resistivity of hybrid film is same after one time tape adhesion test and even after three times tape removal, which can be confirmed by microscope magnified image in the Figure 13.

Table 1. Resistivity of AgNPs film and Hybrid film

Conductive Film's Resistivity		
Tapes time	Ag nano-particle film	Hybrid film
Before	10.1	8.1
1 time	26	8.0
3 times	Over limit	8.1



AgNPs coated film Hybrid Film

Figure 13. Microscope images of AgNPs film and Hybrid Film (100 times magnification)

According to tape test results, we understand that conductive polymer provides not only fusing between the AgNPs line connection but also acting as catalysis to crosslink Ag (PEG) and primer layer. Therefore, hybrid coating is shown a strong adhesion.

4.3 Improve scratch resistance property

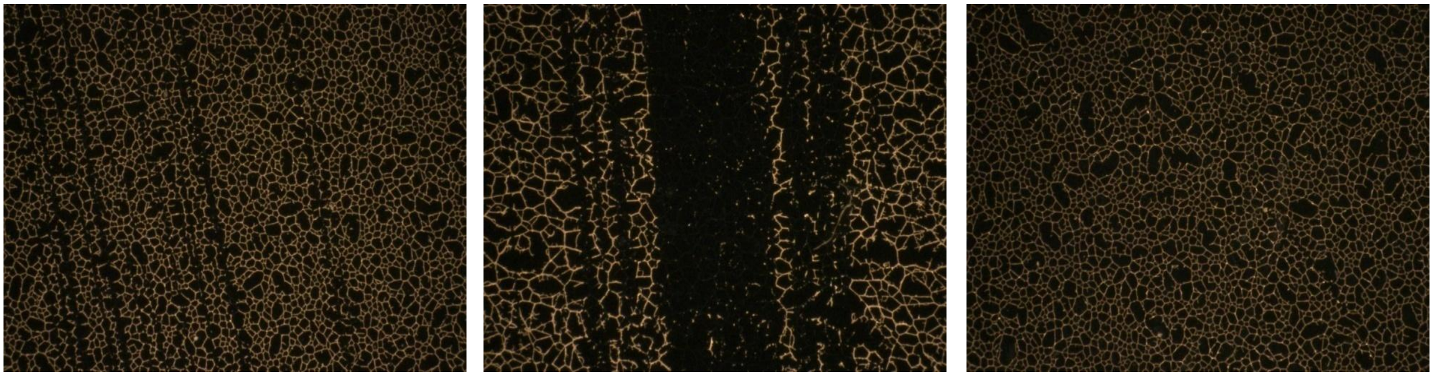
Surface scratch resistance was measured by applying 1000 g of weight on the KIT (tip of the KIT was wrapped by piece of cloth), on the coated surface, and move this weight gently for many times. The resistivity was measured after one time or three times double rubs. The results are shown in the Table 2. The surface resistivity of AgNPs film become unlimited after one or three times double rubs. However, the surface resistivity of hybrid film is not changed after three times double rub cycles. The AgNPs mesh network was scratched off after one time double rubbed, but the mesh of hybrid film is remaining after ten times double rub cycles as showing in the microscope picture in the Figure 14.

The PEDOT:PSS coating acts as the protective layer on the AgNP's film, and provides much stronger cross linking and binding forces through the entire AgNP's networks and to substrate. This result demonstrated strong adhesion of AgNP – PEDOT:PSS film.

Table 2. Scratch test result of hybrid film

Conductive Film's Resistivity				
Double rub cycles	Ag nano-particle		Hybrid film	
	Surface	Ω/inch	Surface	Ω/inch
Before	No scratch	10.1	No scratch	8.0
1 time	Scratched	--	No scratch	8.1
3 times	Come off	Over limit	No scratch	8.0

AgNPs coated film Hybrid film



One time double rub cycles Ten times double rub cycles Ten times double rub cycles

Figure 14. Surface microscope image of AgNP film and hybrid film

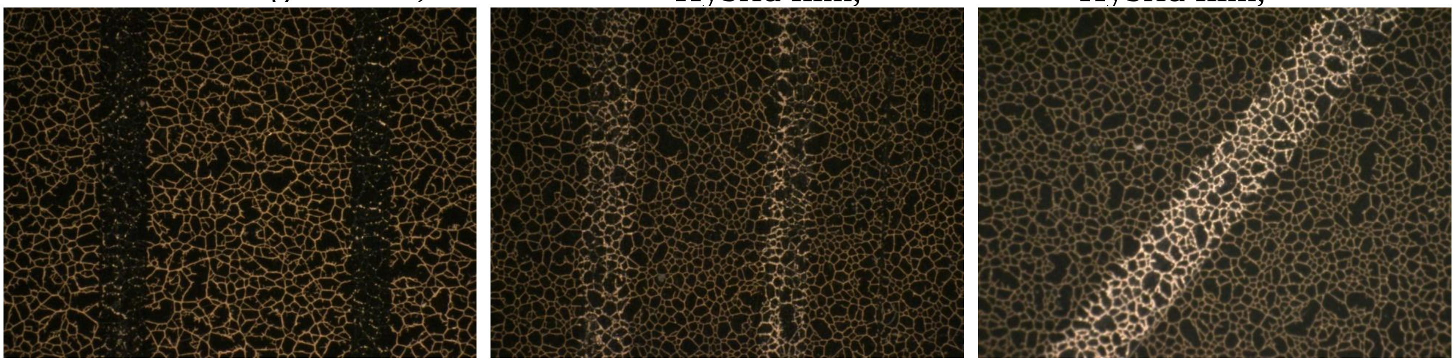
4.4 Improve pencil hardness property

Furthermore, to make sure the strong binding force between AgNPs and substrate induced by PEDOT:PSS, the pencil hardness on surface of hybrid conductive film was tested the results are shown in the Table 3 and Figure 15. The pencil hardness test scratched off the AgNPs line on the AgNPs film. However, hybrid film showed 1H pencil hardness, while durability (500 hours at 60°C 90% humidity; 80°C) tested hybrid film shows 2H pencil hardness. This results show clearly that conductive polymer coating provides strong binding force between the AgNPs and AgNPs to primer layer of the hybrid film.

Table 3. Pencil hardness of AgNPs and hybrid film

Hardness of Film			
Pencil hardness	Ag nano-particle film	Hybrid film	Hybrid 500 Hrs 60°C 90% humidity; 80°C
1H	NG	Pass	Pass
2H	NG	NG	Pass

Ag NP film; Hybrid film; Hybrid film;



Pencil hardness 1H Pencil hardness 1H Pencil hardness 2H

Figure 15. Surface microscope image of AgNP film and hybrid film

4.5 Color property of hybrid film

L*, a*, and b* values were measured on the surface of the hybrid film, the results are shown in Table 4. While increasing amount of CP, L* is decreased slightly because of the weak absorption of PEDOT:PSS in the visible range, and b* and a* value are decreased because the characteristics of conductive polymer.

Table 4. Color property of hybrid film

Color of Hybrid conductive film							**500 hours**	
							80ºC	60ºC 90%H
CP	SANTE	0	4	8	10	12	4	4
L*	82.57	81.90	81.1	79.3	79.4	78.2	80	80
a*	0.42	0.09	-0.23	-0.65	-0.87	-0.95	-0.66	-0.68
b*	2.12	1.63	1.27	0.83	0.42	-0.05	1.02	1.01

The durability of hybrid film was checked at 80℃ and 60℃ 90% humidity for 500 hours, the result is shown in the Table 3 and 4. When hybrid coated film is dried and hydrated, the volume of AgNPs- conductive polymer line is shrink and the AgNPs – PEDOT particles aggregates with much closer parking. We understand this force drive AgNPs and PEDOT closer, these results in tighter contact between AgNPs and AgNPs with PEDOT. Therefore, pencil hardness of 2H is reached after 500 hours at the high temperature and humidity, and the transmittance is slightly decreased.

Conclusion

In conclusion, KTI has fabricated conductive polymer film, and conductive silver nano-particle film, for flexible displays at lower cost, lower resistivity, and higher transmittance and with improved flexibility property by using roll-to-roll process.

The strong adhesion between AgNPs and the substrate is critical to obtain stable and robust AgNP films for variety applications. The coated film's network, transparence, and conductivity was increased when polyethylene oxide functional acrylic monomers was used as primer which bound AgNPs and substrate.

KTI has also developed a hybrid conductive film by using a simple and effective method, and achieved a highly conductive AgNP / conductive polymer composite meshes with excellent optical transparency and mechanical properties. This is achieved via applying PEDOT:PSS solutions sequentially to treat AgNP's films, resulting in AgNP / PEDOT:PSS composites. The conductive polymer acts the protective layer on the AgNP's film, and provides much stronger cross linking and binding forces through the entire AgNP's networks and to substrate. This result demonstrated strong adhesion of AgNP – PEDOT:PSS film. Thin films coated from this composite possess excellent mechanical, electric, and optical properties.

Kimoto's coating technology improves flexible conductive films by supplementing with consistent electrical conductivity, high transparency, durable surfaces, and an attractive appearance. KTI also adds value and functionality by applying a variety of proprietary coatings to plastic substrates on one or both sides. KTI has also developed hard-coated polyester and polycarbonate material offering excellent impact resistance, optical clarity, excellent abrasion resistance, and weather ability.

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