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Effect of rheological properties on the pattern formation in screen printing process

스크린 인쇄 공정에서 유변물성이 패턴의
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Abstract

Effect of rheological properties on the pattern formation in screen printing process

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Screen printing process is used in various areas in the production process of printed circuits, thick film integrated circuits, resistors, capacitors, light-sensitive components and thermal components. TiO_2 paste is used to make titanium dioxide anode which is used in dye sensitized solar cells (DSSC). The effect of paste composition on the pattern formation of TiO_2 electrode was investigated for efficient control and optimization of the main fabrication step of the DSSC. In particular, the effect of binder was focused, and the relationship between the printed patterns and the rheological properties was investigated. The printed patterns were observed using a 3-D confocal laser scanning microscopy. Rheological behavior of the paste was different depending on the binder concentration. Below critical binder concentration (< 2 wt%), there was a strong shear thinning behavior, which causes patterns to be spread. On the other hand, above critical binder concentration (≥ 2 wt%), though there was a slight shear thickening at high shear rate, the viscosity at low shear was much lower and we could obtain clear patterns. Transition of modulus is found near critical binder concentration. Below critical binder concentration (< 2 wt%), storage modulus is higher than loss modulus, on the other hand, above critical binder concentration (≥ 2 wt%), storage modulus is lower than loss modulus which is similar to the tendency of the patterns.

To conclude, by measuring the rheological properties, the relationship between the component of the paste and the

printed pattern could be found, which may result in a better design of the paste with enhanced processability.

Keywords: Screen printing, critical point, binder concentration, particle concentration
Student Number: 2014-21597

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Chapter 1. Introduction

1.1 Screen printing

Screen printing process is used in various areas in the production process of printed circuits, thick film integrated circuits, resistors, capacitors, light−sensitive components and thermal components. Screen printing is used to these areas due to its cost effectiveness. The resolution of the printing lines and spaces are related to many factors, such as the substrate materials performance, the screen performance, the squeegee speed, the squeegee pressure, the distance between screen and squeegee, and the paste rheology and the various parameters of printing process. The process parameters can be optimized by several trial and errors, so they are not limiting factors. However, the paste properties are difficult to control during process, which results in final productivity. The printing process can be divided into four steps. First the paste undergoes shear stress by movement of the scrapper and become viscous liquid, which can be spread to the screen easily. The viscosity approaches to the minimum value when the paste passes through the mesh. Then the mesh is separated from the deposited paste. The modulus increases rapidly after these processes and restore to elastic solid again.

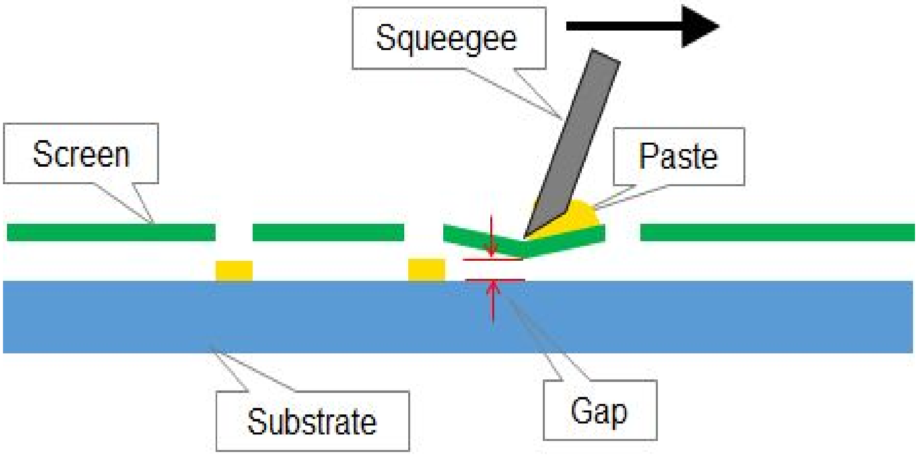


Figure 1 Structure of screen printer

1.2 Paste system

Paste is composed of nanoparticles, polymer binders, solvent, and other additives. Nanoparticles such as titanium dioxide has been used as dye sensitized solar cell for fine line printing, and required particle size for printing is as smaller as possible to get a thinner film. Polymer binder such as ethyl cellulose (EC) is preferred binder in screen printing due to its good affinity with particles and uniform surface properties.

Titanium dioxide paste for inner electrode is composed of various organic additives such as dispersant, solvent, and polymer binders. Paste is a system with high concentration of particles in polymer binder solution, which is required to control the dispersion and the rheological properties. Paste rheology strongly affects the processing condition depending on the factors such as solid contents, particle size and distribution, component composition, mixing process, and correlates well with screen printability. In general, the binder plays an important role in highly filled particle system for dispersion purpose. When the excess amount of binder is used in the paste system, the final film is formed with lower particle density after sintering caused by the porosity of binder burnout. When the amount of binder is not sufficient to disperse the particles, they tend to aggregate resulting in coarse network structure of the paste, which may cause crack or separation during or after drying process. As the role of a binder is important in paste design, there have been many studies on the kinds of polymer binders, different solvent condition, and the effect of dispersant. Polymer binder bridges the particles depending on the affinity of the binder and the particles.

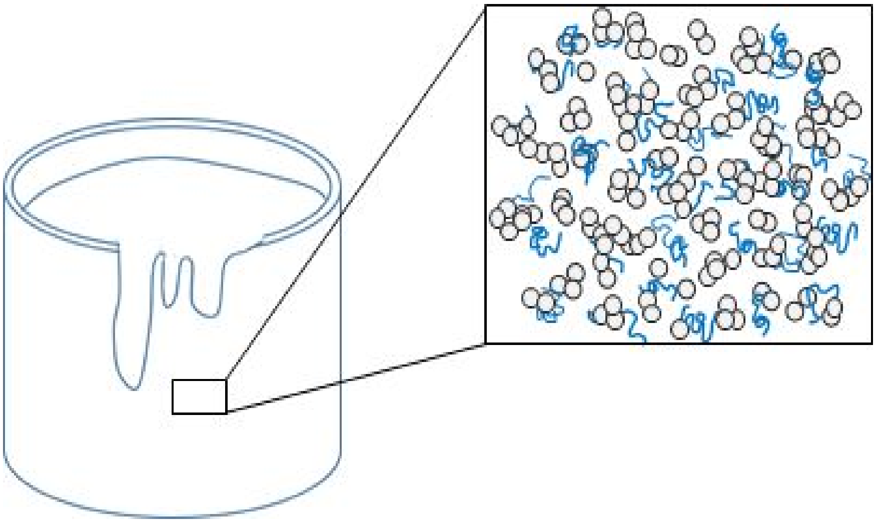


Figure 2 Micro-structure of paste

1.3 Rheological properties of paste

The viscosity is one the most important rheological characteristics of the conducting paste. The conducting paste for screen printing process should show the pseudoplastic behavior which displays a decreasing viscosity with an increasing shear rate. However, to be suitable for screen printing, conducting paste should be somewhat thixotropic in nature. A thixotropic fluid is one in which the shear rate/shear stress ratio is nonlinear. As the shear rate increases, the paste becomes substantially thinner, causing it to flow more readily. The optimum operating viscosity of the paste is dependent on the parameters with the screen printing process. The variations in squeegee speed, squeegee to screen angle, squeegee pressure and snap−off distances will affects the quality of the printed film. If the printed lines have a tendency to spread on standing, it is likely that the viscosity of the paste is too low. Chiu, (2003) in his experiment also noted that the paste viscosity is a significant factor to control the line width including the thickness and roughness of the printed pattern.

Rheological properties of paste represent printing quality because they show information of the flow behavior of paste and its microstructure. To clarify, by adjusting the rheology of the paste flow behavior and final microstructure could be controlled. Quite a few studies have investigated printing paste, mostly focusing on the printing process and suggesting equipment improvements. Only a few authors have seriously investigated the rheology of solder pastes. Most publications only report standard rheological test results and try to correlate these data with printing parameters. No deep investigation was achieved into the material characterization with understanding the interaction between components, viscosity, modulus, thixotropy. The difficulty of predicting the paste flow behavior is due to lack of knowledge of the microstructure of paste and to the complexity of the measurements. To analyze the microstructure of materials, rheological approach is used to confirm dispersion state of the paste.

In this study, the relationship between printed pattern and rheological properties were observed, by changing concentration of particle and concentration of binder. The effect of polymer binder on the dispersion, rheology and printed pattern is discussed.

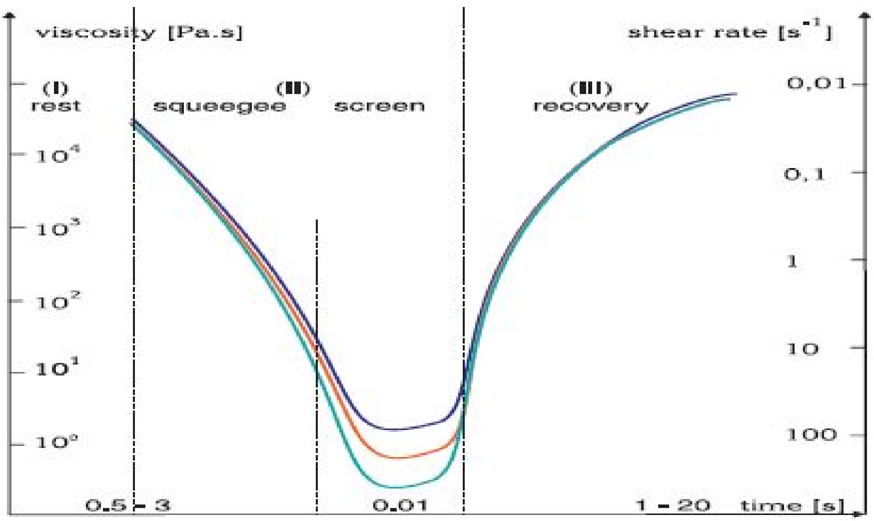


Figure 3 Rheological properties involved in screen printing process

Chapter 2. Experimental

2.1 Materials

A commercial TiO_2 powder (CN-vision, Korea) has mean particle size 10 nm and specific surface area of 280 m^2/g. Terpineol (Sigma-Aldrich) was used as suspending medium. Ethyl cellulose (Sigma-Aldrich) having viscosity 100 cP at 5 % in toluene/ethanol 80:20(lit.) solution was used as a binder. Paste were prepared by adding 25, 35, 45 wt% solid particles into organic solvent with 0, 0.5, 1, 2, 4 wt% polymer binders. The paste in set 1 contain 35 wt% of polymers and set 2 and 3 contain 25 and 45 wt% of polymers. The information of paste composition is summarized at Fig 4.

	TiO_2	Ethyl cellulose	Terpineol
Role	**Particle**	**Binder**	**Solvent**
Paste1	35wt%	0wt%	65wt%
Paste 2	35wt%	0.5wt%	64.5wt%
Paste 3	35wt%	1wt%	64wt%
Paste 4	35wt%	2wt%	63wt%
Paste 5	35wt%	4wt%	61wt%

	TiO_2	Ethyl cellulose	Terpineol
Role	**Particle**	**Binder**	**Solvent**
Paste 6	25wt%	0wt%	55wt%
Paste 7	25wt%	0.5wt%	54.5wt%
Paste 8	25wt%	1wt%	54wt%
Paste 9	25wt%	2wt%	53wt%
Paste 10	25wt%	4wt%	51wt%

	TiO_2	Ethyl cellulose	Terpineol
Role	**Particle**	**Binder**	**Solvent**
Paste 11	45wt%	0wt%	35wt%
Paste 12	45wt%	0.5wt%	34.5wt%
Paste 13	45wt%	1wt%	34wt%
Paste 14	45wt%	2wt%	33wt%
Paste 15	45wt%	4wt%	31wt%

Figure 4 Composition of screen printing paste

2.2 Characterization

2.2.1 Screen printing

The screen printer was equipped and printing was performed at 300mm/s of printing speed with equipped mesh. The gap between mesh and substrate is 1 μm.

2.2.2 Confocal laser scanning microscopy

Printing results were examined by confocal laser scanning microscopy (OLS3000, LEXT) with semiconductor laser (λ=408±5nm*) after drying. A scanning type laser microscope scans in x-y direction. Moreover confocal optics can recognize surface in z-direction by laser that comes from place other than focusing position. Printing surface is observed 3-dimensionally by confocal laser scanning microscopy.

2.2.3 Rheometry

Rheological measurement were performed on controlled stress type rheometer (AR-G2, TA Instrument) at room temperature (25 ℃). Parallel plate geometry was used to measure 25 wt%, 35 wt% TiO_2 paste and gap size was 1mm. And concentric cylinder geometry was used to measure 45 wt% TiO_2 paste and gap size was 5920 μm. Concentric cylinder geometry was used at 45 wt% TiO_2 paste because edge fracture was found at high binder concentration.

2.2.4 Quantification of printed pattern

Quantification factor (F) was defined as area of the printed pattern over area of mesh pattern. If F is closer to 1, patterns are well printed.

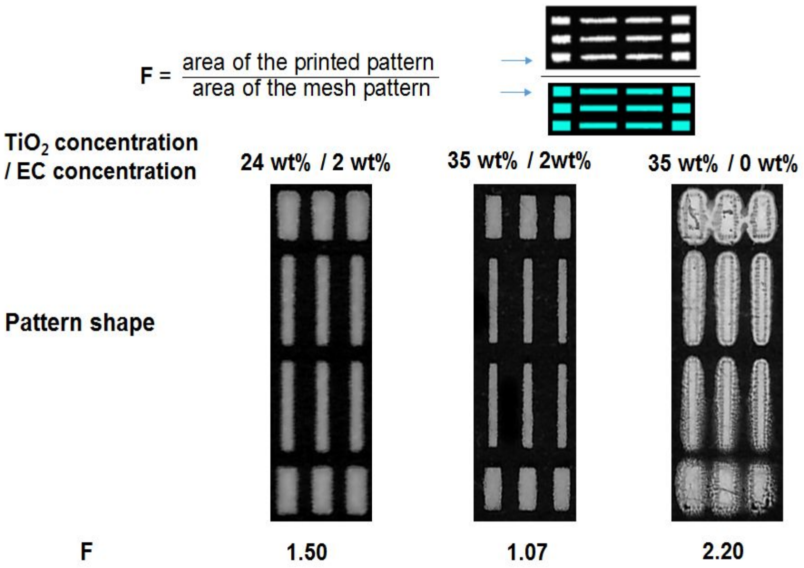


Figure 5 Quantification factor of screen printed pattern

Chapter 3. Results and Discussion

3.1 Printing surface

3.1.1 Macro-pattern

Before analyzing the results of confocal microscopy, we need to confirm the macro-pattern because its overall tendency can be seen visually. Fig 6 shows how pattern is spread after screen printing.

3.2 Effect of particle concentration on printed pattern

3.2.1 Macro−pattern

The effect of particle concentration on printed pattern can be seen by observing macro−pattern. By increasing the concentration of particle, F (quantification factor) decreases which means patterns are less spread.

3.2.2 Rate sweep test

The viscosity was measured in descending order with sufficient equilibrium delays to reach steady state. Printed patterns are compared with same concentration of binder (2 wt%). If the particle concentration lower than 35 wt%, sufficient viscosity level is not obtained. Due to lower viscosity, quantification factor (F) is far from 1, which means patterns are not clearly printed.

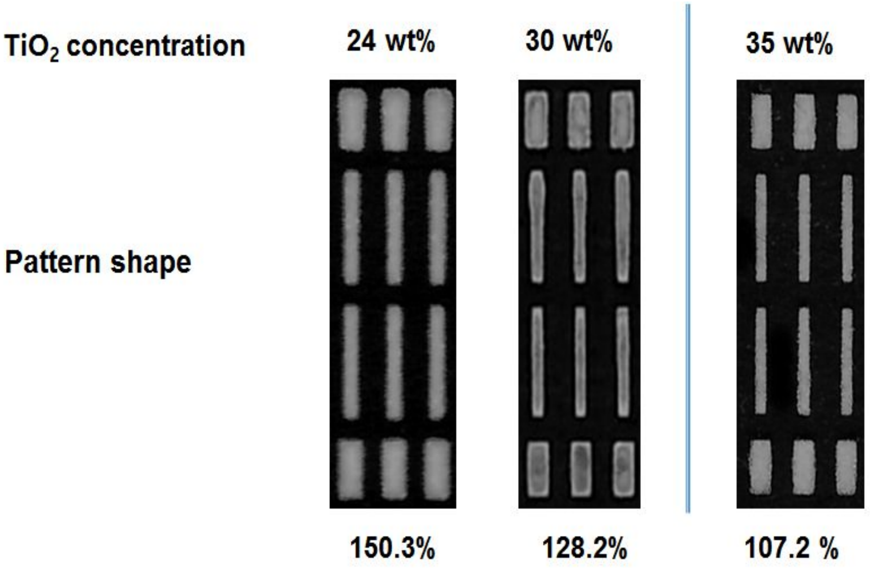


Figure 6 Effect of particle concentration on screen printed pattern

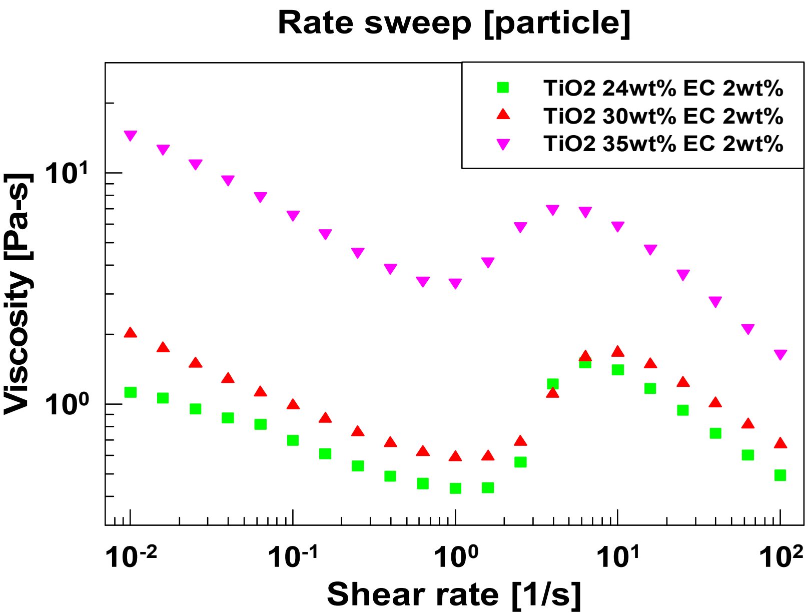


Figure 7 Effect of particle concentration on viscosity

3.2.3 Frequency sweep test

Modulus level differs from 35 wt% and under 35 wt%. But no significant change was found by changing concentration of particle.

3.3 Effect of binder concentration on printed pattern

3.3.1 Macro-pattern

The effect of binder concentration on printed pattern can be seen by observing macro-pattern. By increasing the concentration of binder, F (quantification factor) decreases which means patterns are less spread. Dramatic change in printed pattern shows transition between 1 wt%

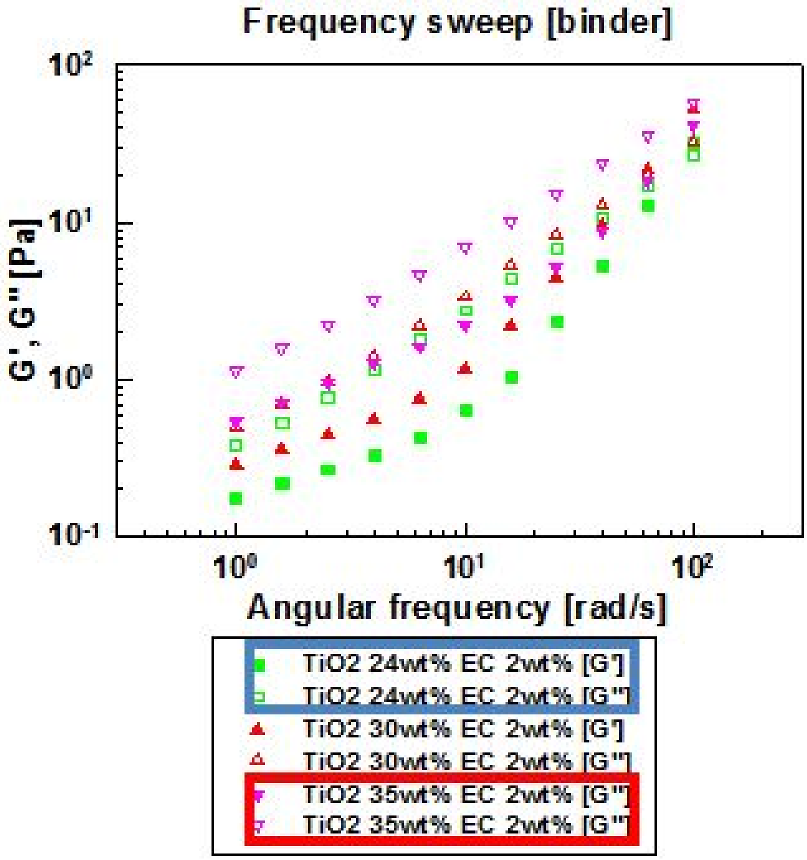


Figure 8 Effect of particle concentration on modulus

and 2 wt% of binder concentration.

3.3.2 Rate sweep test

The viscosity was measured in descending order with sufficient equilibrium delays to reach steady state. Printed patterns are compared with same concentration of particle (35 wt%). Concentration of binder under 2 wt% shows shear thinning behavior, however, concentration over 2 wt% shows shear thickening behavior at low shear.

Fig 11 shows viscosity at shear rate= $0.1s^{-1}$ by changing concentration of binder. Dramatic change in viscosity shows transition between 1 wt% and 2 wt% of binder concentration.

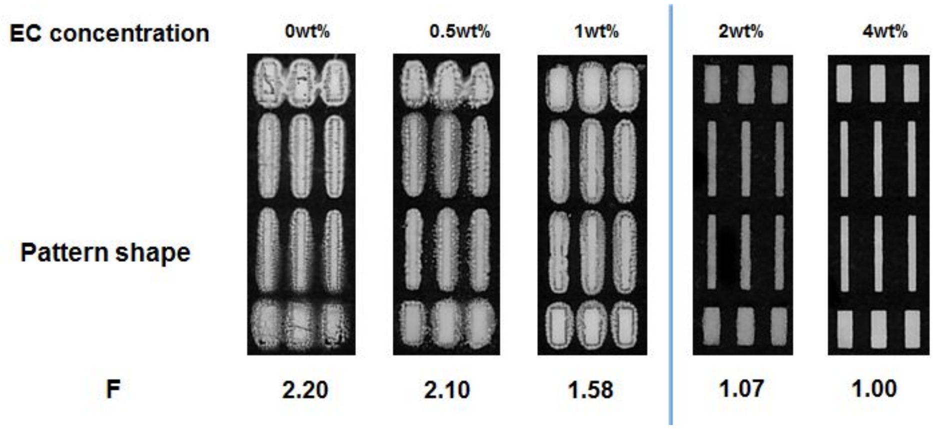


Figure 9 Effect of binder concentration on screen printed pattern

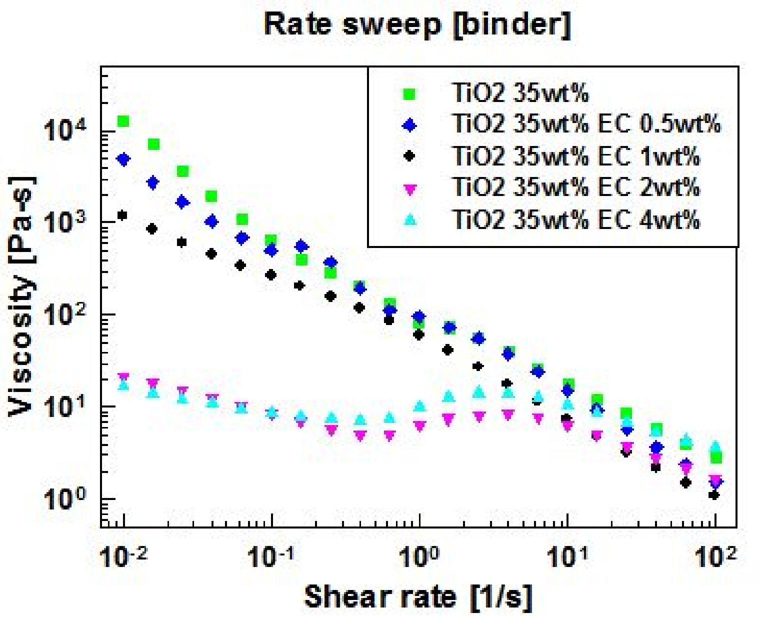
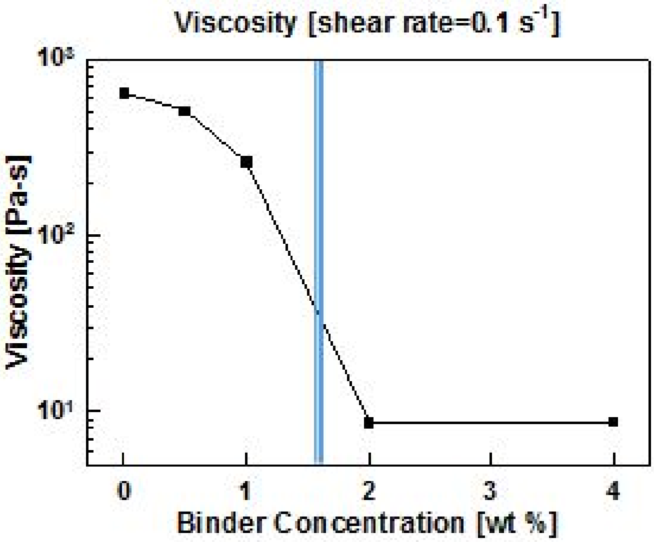


Figure 10 Effect of binder concentration on viscosity



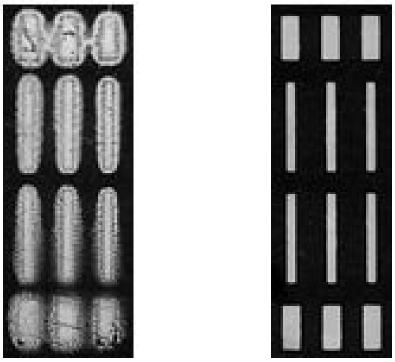


Figure 11 Viscosity at shear rate= $0.1s^{-1}$ by changing concentration and printed pattern

3.3.3 Frequency sweep test

Modulus level differs from over 2 wt% and under 2 wt%. If the concentration of binder is under 2 wt%, storage modulus is higher than loss modulus. However, binder concentration over 2 wt%, loss modulus is higher than storage modulus.

Fig 13 shows modulus at frequency= 1 rad/s by changing concentration of binder. Dramatic change in modulus shows transition between 1 wt% and 2 wt% of binder concentration. Therefore critical point exist between 1 wt% and 2 wt% of binder concentration at concentration of particle 35 wt%. The rheological properties such as viscosity and modulus and printed pattern shows same tendency. We will focus on investigating the effect of binder and particle among various factors in order to know what effect printing qualities.

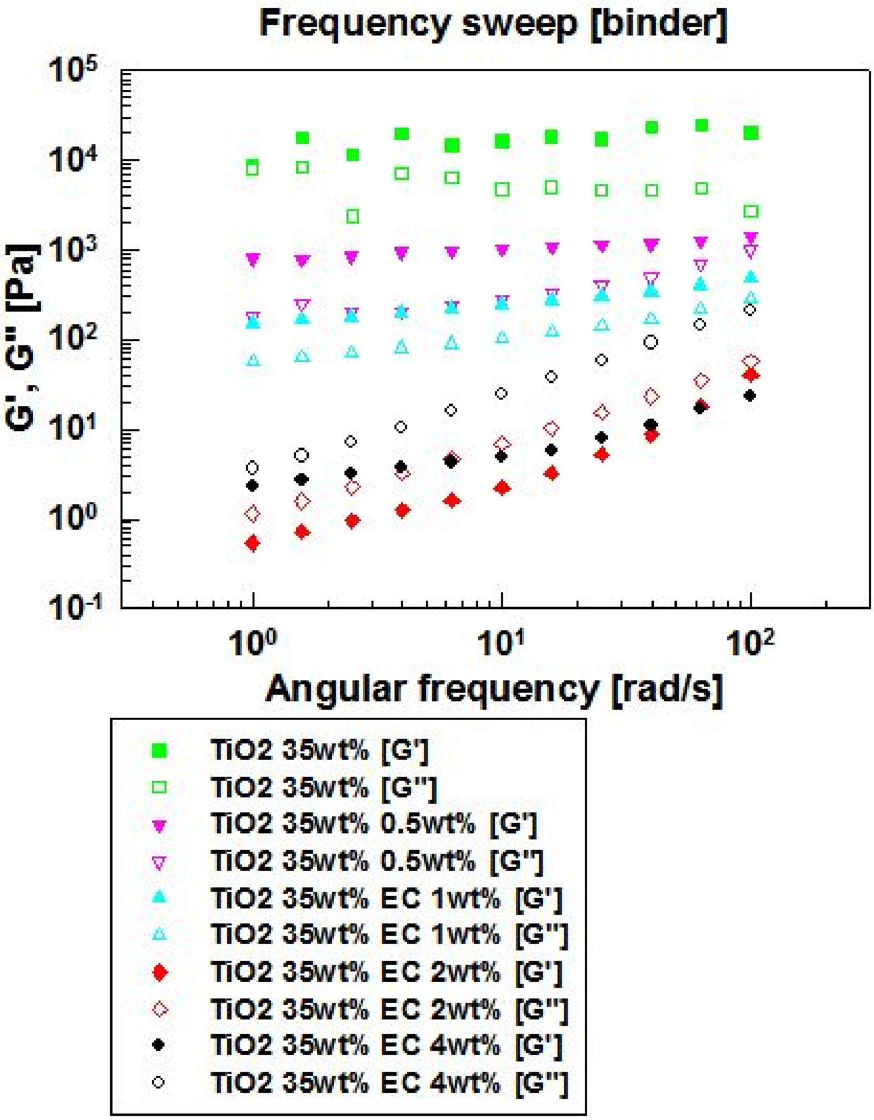


Figure 12 Effect of binder concentration on modulus

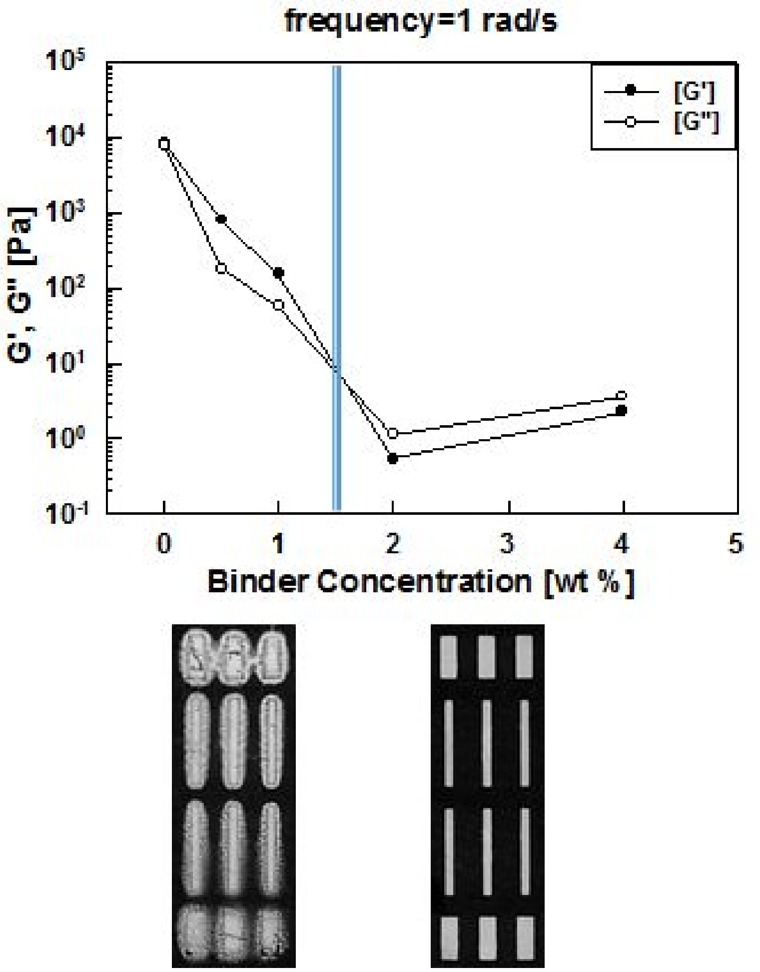


Figure 13 Modulus at frequency= 1 rad/s by changing concentration of binder

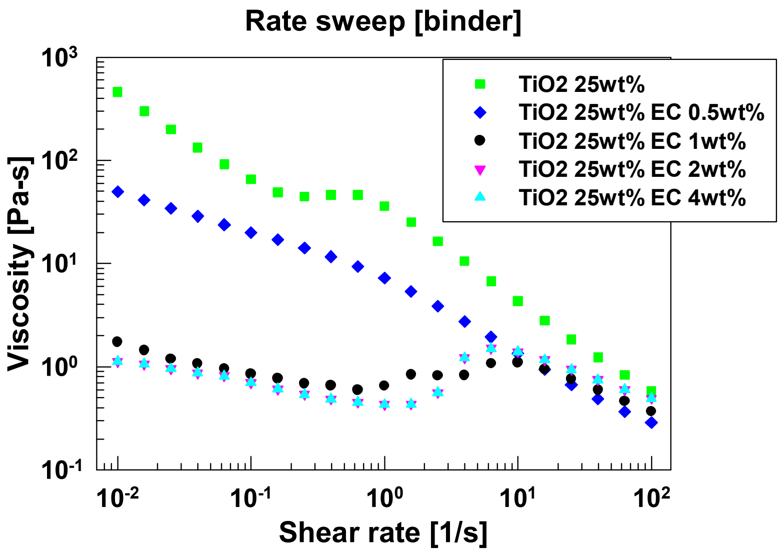
3.4 Effect of particle & binder concentration on printed pattern

In order to investigate the effect of particle and binder, changing the concentration of particle and binder is needed. So same investigation on particle 25 wt% and 45 wt% were observed.

3.4.1 Effect of binder concentration at particle concentration 25 wt%

At concentration of particle 25 wt%, F (quantification factor) decreases which means patterns are less spread. The viscosity was measured in descending order with sufficient equilibrium delays to reach steady state which is same condition with concentration of particle 35 wt%. Printed patterns are compared with same concentration of

(a)



(b)

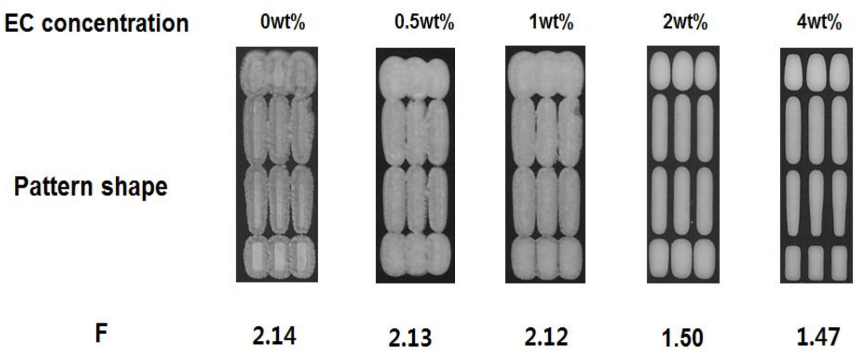


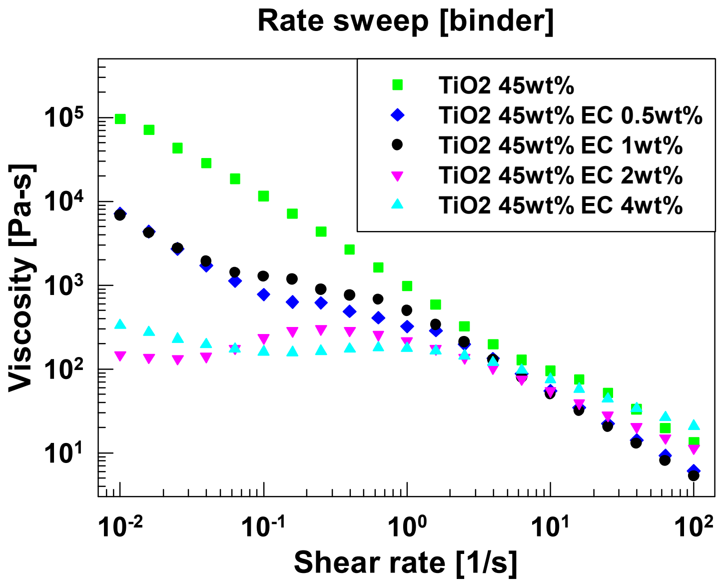
Figure 14 Effect of binder concentration on (a) viscosity (b) printed pattern at particle concentration 25 wt%

particle (25 wt%). Concentration of binder under 1 wt% shows shear thinning behavior, however, concentration over 1 wt% shows shear thickening behavior at low shear. Dramatic change in viscosity shows transition between 0.5 wt% and 1 wt% of binder concentration.

3.4.2 Effect of binder concentration at particle concentration 45 wt%

At concentration of binder 45 wt%, F (quantification factor) decreases which means patterns are less spread. Dramatic change in printed pattern shows transition between 1 wt% and 2 wt% of binder concentration. The viscosity was measured in descending order with sufficient equilibrium delays to reach steady state which is same condition with concentration of particle 25 wt%. Concentration of binder

(a)



(b)

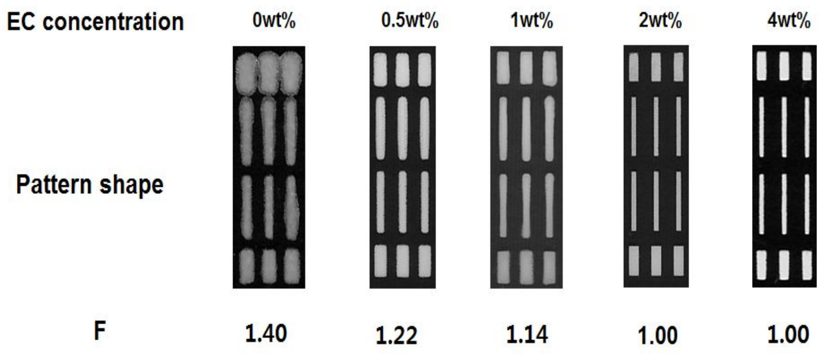


Figure 15 Effect of binder concentration on (a) viscosity (b) printed pattern at particle concentration 45 wt%

under 2 wt% shows shear thinning behavior, however, concentration over 2 wt% shows shear thickening behavior at low shear.

3.4.3 Effect of viscosity on printed pattern

Fig 16 shows viscosity at shear rate= 0.01 s^{-1} by changing concentration of binder and concentration of particle. To observe the effect of binder and particle, binder/particle ratio was considered. If the ratio of binder/particle is over 0.04, patterns were well printed. However, the ratio of binder/particle is under 0.028, patterns were not well printed. Also, if viscosity at shear rate= 0.01 s^{-1} is over 10 pa−s, patterns were well printed. But, viscosity at shear rate= 0.01 s^{-1} is under 10 pa−s, patterns were not well printed. Therefore, transition exist between binder/particle 0.028 and 0.04, certain amount of binder is needed to acquire well dispersed paste. Moreover,

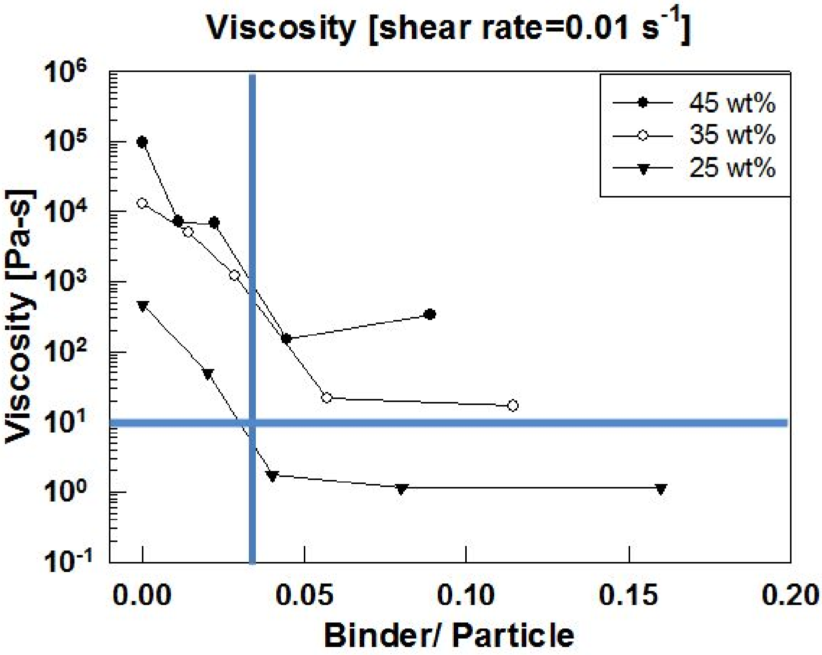


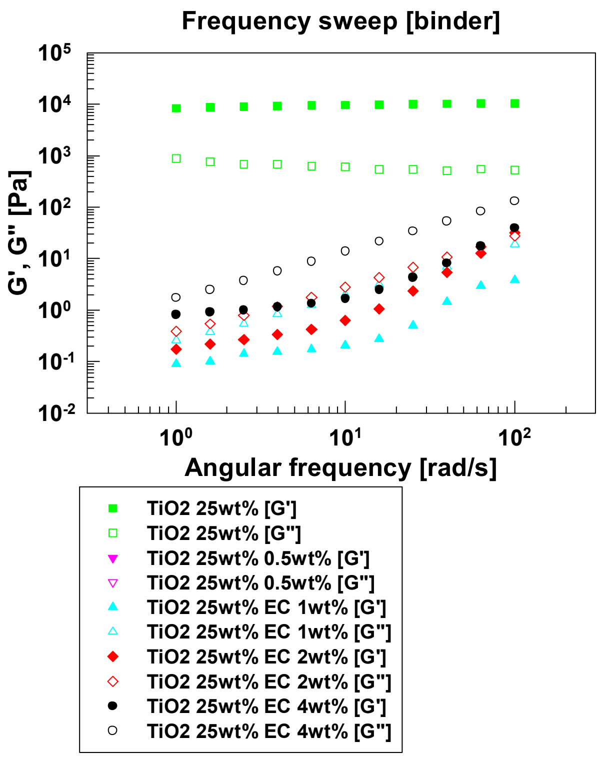
Figure 16 Effect of binder and particle ratio to viscosity

viscosity at low shear rate has to be considered to acquire clear pattern.

3.4.4 Effect of modulus on printed pattern

Fig 19 shows storage modulus and loss modulus at frequency = 1 rad/s by changing concentration of binder and concentration of particle. To observe the effect of binder and particle, tangent delta has been considered. If the ratio of binder/particle is over 0.04, patterns were well printed. However, the ratio of binder/particle is under 0.028, patterns were not well printed. Dramatic change in tangent delta shows transition between binder/particle 0.028 and 0.04. Same tendency has been observed with viscosity and tangent delta.

(a)



(b)

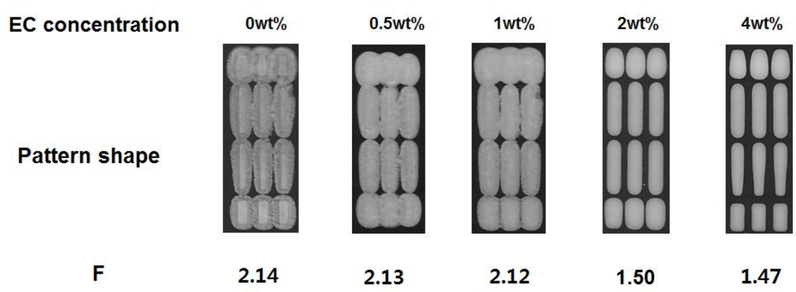
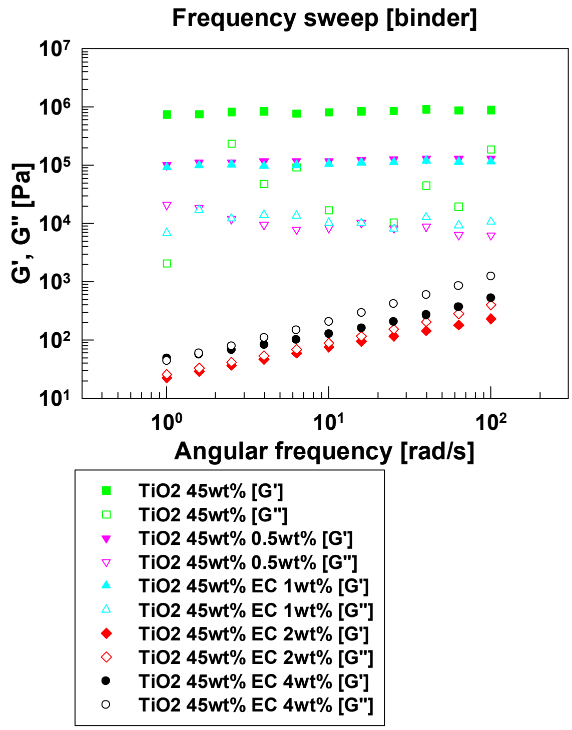


Figure 17 Effect of binder concentration on (a) modulus (b) printed pattern at particle concentration 45 wt%

(a)



(b)

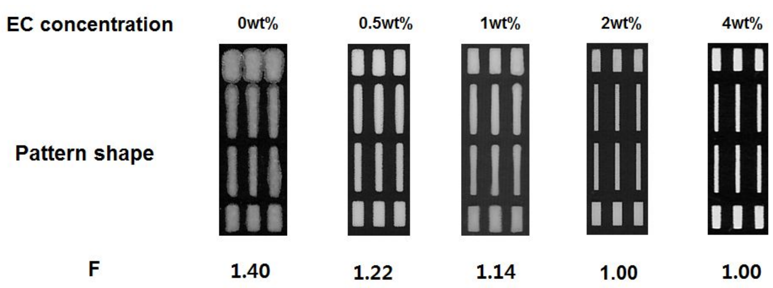


Figure 18 Effect of binder concentration on (a) modulus (b) pattern at binder concentration 45 wt%

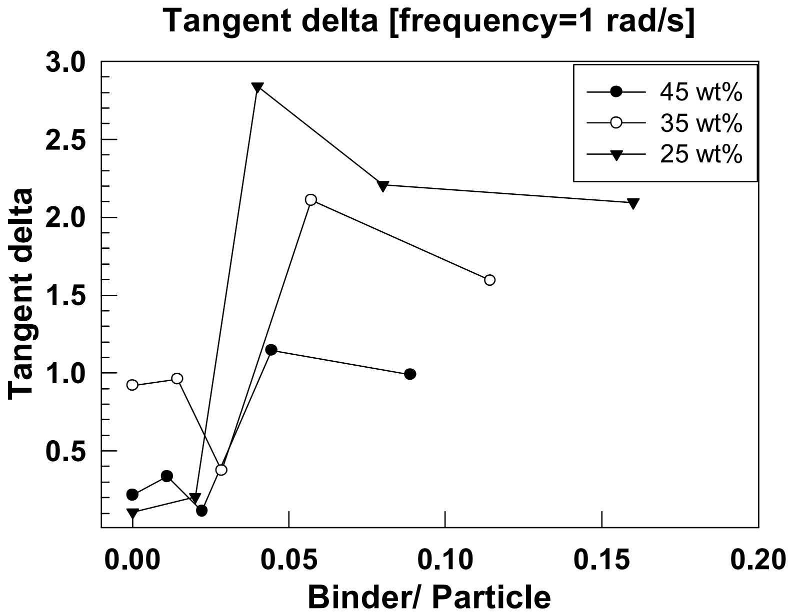


Figure 19 Effect of binder particle ratio to tangent delta

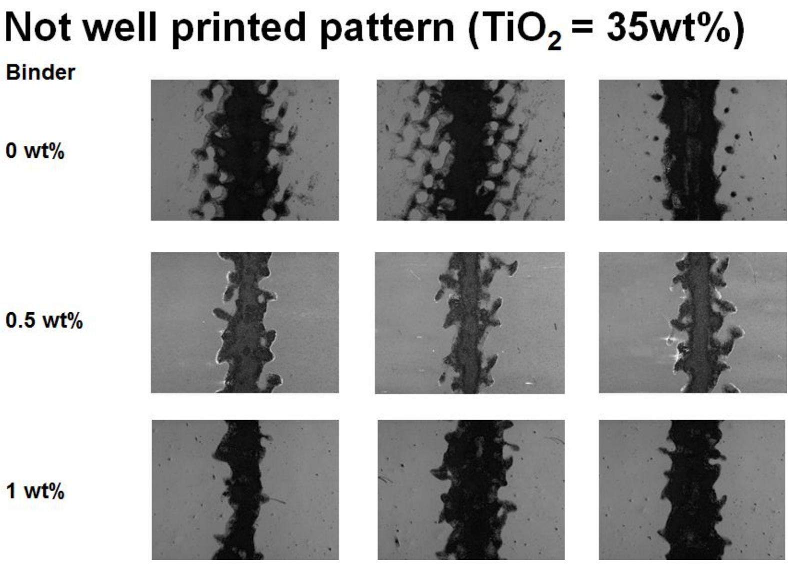
3.5 Confocal laser scanning microscopy

Optical information of confocal laser scanning microscopy could confirm configuration of surface profile. 1-D surface profiler(Alpha step) has a good resolution of 0.1 nm in z-direction and 0.01 μm in x-y direction. The 1-D profile which is obtained from confocal laser scanning microscopy is in good agreement with real pattern profile.

3.5.1 Micro-pattern

The width of the micro-patterns are 50 micro meter. The printing surfaces of the prepared pastes were observed from 2D-image in which intensity of picture at each point has a linear relation with the

(a)



(b)

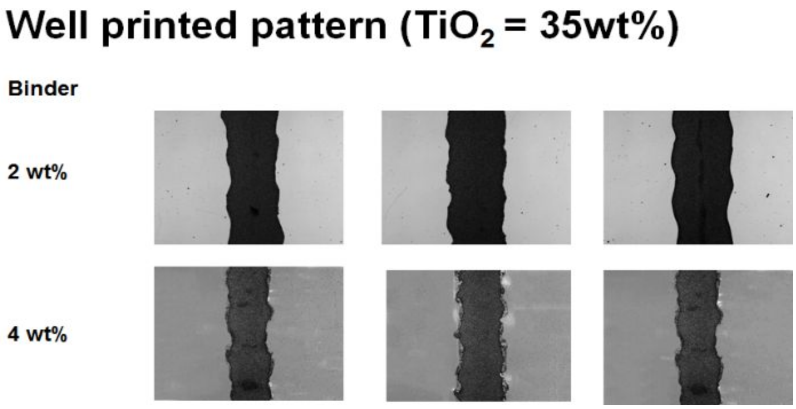


Figure 20 Effect of binder concentration on (a) not well printed micro−pattern (b) well printed micro−pattern

height of surface. At concentration of particle 35 wt%, binder concentration under 2 wt% shows various behavior, which means patterns are not uniformly printed. However, binder concentration over 2 wt% is uniformly printed. Same tendency has been observed with macro-patterns, viscosity, and modulus.

Length and height of well printed micro-patterns were quantified by using confocal laser scanning microscopy surface profile method. If the concentration of particle is 35 wt%, width of binder concentration 4 wt% is smaller than that of binder concentration 2 wt%, which means patterns are less spread. Also, height of binder concentration 4 wt% is larger than that of binder concentration 2 wt%.

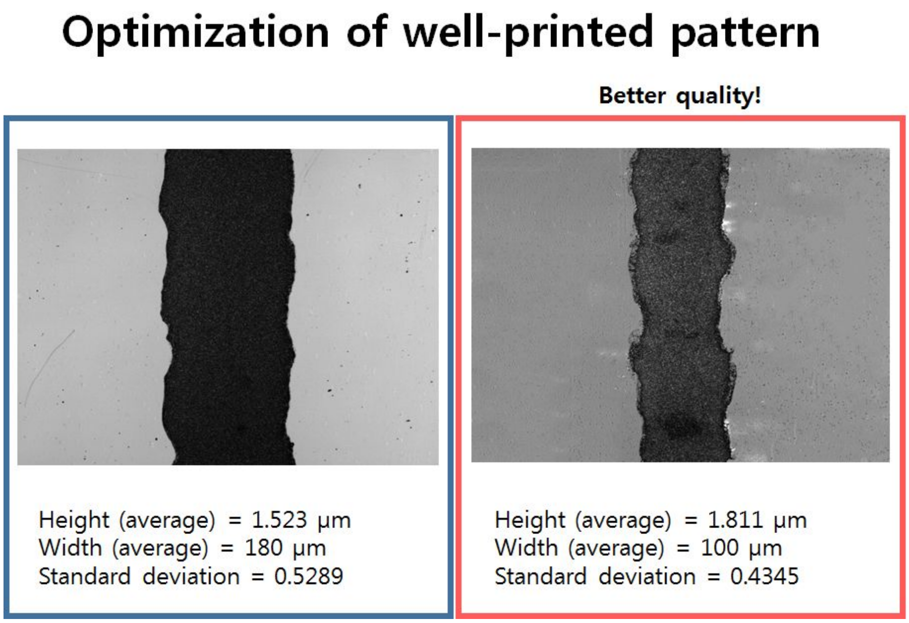


Figure 21 Optimization of well printed pattern

Chapter 4. Conclusions

Surface of screen printing was quantified, and matched with rheological properties of screen printing paste. Investigating macro-pattern is needed to observe the tendency of micro-pattern easily. Concentration of particle, concentration of binder and ratio of binder/particle could be factors of surface quality of printing. Poor quality of patterns can be observed when the concentration of binder is under transition point and low shear viscosity is under critical point. It could be confirmed by steady state flow sweep and oscillatory frequency sweep in this system.

From the results, considering low shear viscosity and binder/particle ratio is needed to obtain uniform printing surface and it could be confirmed by rheological properties.

References

1. T. A. Nguty, N. N. Ekere, and A. Adebayo, IEEVCPMT Int'l Electronics Manufaduring Technology Symposium, 1999, pp. 304−312.

2. Durairaj R., G.J. Jackson, N.N. Ekera, G. Glinski and C. Bailey, Soldering & Surface Mount Technology 2002;14(1) 11-17.

3. Durairaj R., A. Seman and N.N.Ekere, Electronics Systemintegration Technology Conference, 2006. pp 348−353.

4. Kun Cao, Kai Cheng, Ziliang Wang, 7th International Conference on Electronics Packaging Technology, 2006.

5. Catherine Billotte, Pierre J. Carreau, Marie−Claude Heuzey, Rheol Acta 2006;45: 374-386.

6. S. Mallik, J. Thieme, R. Bauera, N. N. Ekere, A. Seman, R. Bhatti and R. Durairaj, 11th Electronics Packaging Technology Conference 2009, pp. 869−874.

7. Amalu, E.H., Ekere, N.N. & Mallik, S. (2011), Materials and Design, Vol. 32, (February 2011), pp. 3189-3197.

8. Burnside, S., Winkel, S., Brooks, K., Shklover, V., Gratzel, M., Hinsch, A., Kinderman, R., Bradbury, C., Hagfeldt, A. & Pettersson, H., Journal of Materials Science: Materials in Electronics, Vol. 11, 2000, pp. 355-362.

9. Buzby, D. & Dobie, A, Proceedings of the 41st International Symposium on Microelectronics (IMAPS 2008), Rhode Island, USA, November 2008.

10. Chiu, K.-C, Process of the International Joint Conference on Neural Network. Vol.2, 2003. pp. 1043-1047.

11. Durairaj, R, Ekere, N.N. and Salam, B, J. Mater. Scie: Mater Electron., Vol. 15, 2004. pp. 677-683.

12. Durairaj, R., Mallik, S., Seman, A. & Ekere, N.N. (2009a), Sadhana, Vol. 34, No.5, 2009, pp. 799-810.

13. Durairaj, R., Ramesh, S., Mallik, S., Seman, A. & Ekere, N.N, Materials and Design, Vol. 30, 2009. pp. 3812-3818.

14. Evans J.W. & Beddow, J.K, IEEE Trans. Compo. Hybrids Manufac. Tech., 1987, pp. 224-231.

15. Gilleo, K. Screen Printing, 1989, pp.128-132.

16. Hoornstra, J., Weeber, A.W., Moor, H.H.C. & Simke, W.C, Proceedings of 14th EPSEC, Barcelona, 1997, pp. 823-826.

17. Kardashian, V.S. & Vellanki, S.J.R. Hybrids and Manufac. Tech. Vol. CHMT-2, No. 2, 1979, pp. 232-239.

18. Lin, H.-W., Chang, C.-P., Hwu, W.-H. & Ger, M.-D, Journal of Materials Processing Technology, Vol. 197, 2008, pp. 284-291.

19. Mallik, S., Thieme, J., Bauer, R., Ekere, N.N., Seman, A., Bhatti, R. & Durairaj, R, Proceedings of the 11th Electronics Packaging Technology Conference, Singapore, 2009, pp. 869-874.

20. Phair, J.W. & Kaiser, F.-J, Annual Transactions of the Nordic Rheology Society, Vol. 17, Iceland, 2009.

21. Rane, S.B., Seth, T., Phatak, G.J., Amalnerkar, D.P. & Ghatpande, M, Journal of Materials Science: Materials in Electronics, Vol. 15, 2004, pp. 103−106.

22. Shin, D.−Y., Lee. Yongshik. & Kim, C.H. Thin Film Solids, 2009, pp. 6112−6118.

23. Shiyong, L., Ning, W, Wencai, X and Yong, L, Materials Chemistry and Physics 111, 2008, pp. 20−23.

24. Webster, R, IEEE Trans. On Manufac. Tech. Vol. MFT−4, No. 1, 1975, pp. 14−20.

25. Yin, W., Lee, D.−H., Choi, J., Park, C. & Cho, S.M, Korean Journal of Chemistry Engineering, Vol. 25, No. 6, 2008, pp. 1358−1361.

초 록

스크린 인쇄는 인쇄 회로, 필름 중첩 회로, 저항, 축전기, 감광성 물질, 열 감지형 물질 등의 생산 등 다양한 분야에 이용되고 있다. 이산화 티타늄 페이스트는 DSSC 용 이산화 티타늄 음극을 만드는데 사용이 된다. 페이스트 조성이 이산화 티타늄 전극의 패턴 형성에 주는 영향은 DSSC에서 효율적인 조절과 주요 제조 공정의 최적화를 위하여 연구되어 왔다. 특히, 바인더의 효과가 주로 부각되었고, 인쇄 패턴과 유변물성의 관계가 연구되어 왔다. 인쇄 표면은 공초점 현미경을 통해 3차원으로 형상화 되었고, 전자 현미경을 통해 관찰되었다. 페이스트의 유변물성은 바인더 함량에 따라 달라졌다. 임계 바인더 함량 아래에서는 강한 전단 박화 현상이 일어나고, 패턴이 퍼진다. 그러나 임계 바인더 함량 이상에서는 낮은 전단 속도에서 점조화가 일어나기는 하지만, 낮은 전단 속도에서 점도가 훨씬 낮고 명확한 패턴이 확보된다. 모듈러스에서의 변화도 임계 바인더 함량 부근에서 관측된다. 임계 바인더 함량

이하에서는 점성이 탄성보다 높지만, 임계 바인더 함량 이상에서는 점성이 탄성보다 낮고 이는 패턴의 경향성과 일치한다. 결론적으로, 유변물성을 측정함으로써 인쇄 패턴과 페이스트의 조성간의 상관관계를 확보할 수 있고, 이를 통해 더 나은 페이스트 디자인을 할 수 있으며, 이는 공정개선에 기여한다.

주요어: 스크린 인쇄, 임계 점, 바인더 함량, 입자 함량

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