셀룰로오스를 이용한 전도성 페이스트의 개발

김 태 현*
이스트만 화학 및 인천대학교 화학과
(2006. 11. 4 접수)

Novel Conductive Paste based on Cellulose Acetate Butyrate

Tae-Hyun Kim*

Eastman Chemical Company, Kingsport, TN 37662, USA
Department of Chemistry, University of Incheon, Dowha-dong 177, Nam-gu, Incheon 402-749, Korea
(Received November 4, 2006)

요 약. 고분자를 바탕으로 한 전도성 페이스트는 전원과 기기를 연결하는 전도 통로를 제공하여 준다. 이러한 전도성 페이스트는 고분자 바인더와 전도성 금속의 두 부분으로 이루어져 있다. 본 연구에서는 낮은 점도와 우수한 금속 피막성을 가지는 셀룰로오스 아세테이트 부타이레이트를 바인더로 사용하여 새로운 전도성 페이스트를 개발하였다. 전도도 측정 결과 안정된 전도도를 보였을 뿐 아니라, 균일한 코팅성과 유연성을 나타내었다.

주제어: 전도성 페이스트, 셀룰로오스, 전도도, 퍼콜레이션 포인트

ABSTRACT. Polymer-based electrically conductive pastes have been used to make the conductive paths between voltage sources and devices. The pastes used for these applications consist of two main components: a polymer binder and a conductive filler. Having both low viscosity and good metal-encapsulating properties, cellulose acetate butyrate (CAB) was regarded to be a good candidate as a binder for the conductive paste. We have prepared a formulation for a novel conductive paste based on CAB. Preliminary studies showed that this conductive paste revealed stable conductivity, together with uniform coating and flexibility.

Keywords: Conductive Paste, Cellulose Acetate Butyrate, Conductivity, Percolation Point

INTRODUCTION

Conductive paths between voltage sources and devices are the key for constructing electronic circuits. While traditional rigid and flex circuits use solid metals, mainly copper, and solid metal solders to attach components to the conductive paths, polymer-based electrically conductive pastes are being used to make the conductive paths.[1,2] Polymer-based conductive pastes offer distinct advantages over conventional solid metals or solder alloys, including reduced package size and thickness, improved proce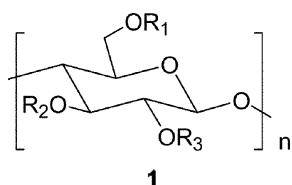ssibility, and lower assembly temperature. The pastes used for these applications consist of two main components: a polymer binder and a conductive filler. The binder is required to hold the conductive filler particles together and to make the filler stick to the substrate. In conductive pastes, the binder is usually a thermoplastic material, which can be dissolved in solvent. The majority of conductive pastes use silver as the conductive metal filler. Much less expensive, but with similar conductivity, metals such as copper experience an increased resistance greatly over the time due to the formation of copper oxide, upon exposure to oxygen, which is not very conductive. The higher resis-

tance in conductive pastes as compared to pure metals is ascribed to the fact that electron encounters tremendous resistance when it has to jump from one metal particle to another. In order to minimize the resistance in conductive pastes, it is essential to optimize the amount of surface contact area between metal particles.

Most significant phenomenon which contributes to the conductivity of polymer-based conductive systems is the 'percolation point', where some of the metal particles begin to contact one another, creating a conductive path. After this point, addition of small amounts of metal filler will produce a rapid drop in resistance. Continued addition of metal filler will eventually reach a point where the resistance levels off, and not much improvement in the conductivity will be obtained even with increased loading of the metal filler. Therefore, good formulations of conductive pastes will use an optimal metal configuration, preferably flake-shaped, at a loading toward the bottom of the percolation point curve. It is the key in this field of study to lower this percolation point (PP), due to the high cost of silver, and to achieve stable conductivity.

Cellulose esters are nontoxic materials widely used as coating layers, fibers, films and additives.[3-6] Recent study to prepare ultrathin films using cellulose for biomedical application was also reported.[7] We were interested in using cellulose acetate butyrate (CAB) 1 as a binder

to prepare a new conductive paste. Due to the good film-forming properties, together with its low viscosity, CAB was regarded as a good candidate for the conductive paste. Focused on the CAB effect as a binder, this paper also broadly covers other components for a conductive paste.

1

R₁, R₂, R₃ = Acetyl, Butyryl, or H

Structure1 1.

EXPERIMENTAL

Sample Preparation

Polymeric binder of choice, was dissolved in analytical grade methyl ethyl ketone (MEK) (unless otherwise mentioned) containing the additives (leafing agent and plasticizer), if required, at the desired concentration. The solutions were left to shake vigorously for 5 min at r.t. before the appropriate metal filler was added. The heterogeneous solutions were again allowed to be well-mixed under the shaker for at least 5 min to assure uniform consistency. The solutions were then applied to the polyester substrate by drawdown technique (wet film deposit of *ca.* 50 μm) and dried at r.t. for 5 min, followed by oven-dry at 90 °C for 90 min. The binder/filler ratio is the weight % ratio between the polymer binder and the metal (silver) filler. All the non-volatiles including additives were considered as a binder. The silver metal fillers were obtained from Metalor in three different forms; flake, particle and powder. The silver flake has the size distribution between 1 and 8 μm, silver powder has the size distribution between 0.4 and 4 μm with the mean value of 1.2 μm, and silver particle has the sizes of ca. 50% with less than 7.3 μm and 90% with less than 16.3 μm. Cellulose acetate butyrate (CAB) 551-0.2, 381-0.1 and 551-0.01 were commercially available products from Eastman chemical company. Dibutyl phthalate and zinc stearate were obtained from Aldrich. Poly(methyl methacrylate) (PMMA) with molecular weight (M_n) of 40,000 and glass transition temperature (T_g) of 105 °C was obtained from Dianal America (brand name: BR-83). Poly(butyl methacrylate) (PBMA) with molecular weight (M_w) of 337,000 and glass transition temperature (T_g) of 15 °C was obtained from Aldrich. Poly(butyl methacrylate-*co*-methacrylate) [P(BMA-*co*-MMA)] with molecular weight (M_w) of 100,000 and glass transition temperature (T_g) of 64 °C was obtained from Aldrich. Film deposition, drawdown speed, drying time and conductivity measurement for all the samples were carried out under the same conditions.

Electric Measurement

The electrical conductivity was investigated by measuring the surface resistance (Ω/cm^2) of the films according to the conventional four-terminal method using aluminum foil electrodes.[8] The resistance across the top layer of the prepared films was measured by placing two electrodes (positive and negative) connected to an ohmmeter with a fixed distance on the surface of a conductive film. The measurement was carried out at three different places with the same distance and the average was taken as a surface resistance of the prepared conductive film. It should be noted that for most cases the film thickness of the conductive film was not considered because the same Meyer bar was used for the film formation and the resistance of the films within the experimental range of thickness (25 to 75 μm of wet film deposit) revealed no difference with the variation of the film thickness. The percolation point was regarded as the point of metal filler/binder ratio where the surface resistance (Ω/cm^2) of the measured dried film surpassed 1. For example, if the resistance was measured as 1 for the sample with filler/binder ratio of 40/60, the percolation point was taken as 40.

RESULTS AND DISCUSSION

Silver Type

It is generally known that the preferred silver filler size for the conductive paste application is between 1 and 30 μm: below 1, electrical properties are adversely affected and above 30, the composition will be too difficult to be applied onto the substrate.[9] All the metal fillers used for our experiments had the average size distribution within this desired range. Samples with different silver forms (flake, particle and powder) were prepared at the fixed silver/binder ratio of 66/34 (wt.%) using CAB 551-0.2 as a binder and MEK as a solvent, and their resistance was measured (*Table* 1).

As the films prepared using silver flake and powder showed much better conductivity (lower resistance) than those from silver particle at this initial silver filler/binder ratio, further electric measure-

Table 1. Conductivity of the films prepared from three different types of silver at the filler/binder ratio of 66/34 using CAB 551-0.2 as a binder

Silver Type	Silver Content [a](wt.%)	Resistance (Ω/cm^2)
Flake	66	5.0×10^{-2}
Particle	66	> 1
Powder	66	8.1×10^{-2}

[a](wt.%) = [silver(g) / (silver(g) − binder(g))] × 100%.

ment for both silver flake and powder was carried out at various silver/binder ratios using CAB 551-0.2 as a binder. The concentration of the total solids (CAB and silver) was set to 72.4 wt.%. As shown in *Table* 2 and *Table* 3 (and also in *Fig.* 1), better conductivity (lower resistance), with lower percolation point (60 for silver powder and 56 for silver flake), was obtained for silver flake. This was consistent with the assumption that a flattened metal flake configuration would increase the area of metal contact, resulting in more conduction paths compared to the contact point generated from either metal powder or particle.[10] From the above results, it was concluded that metal configuration has a sig-

Table 2. Conductivity of the films prepared from silver powder/CAB 551-0.2 in MEK solution

CAB (g)	Silver Powder [g [a](wt.%)]	Resistance (Ω/cm^2)
1.85	6.55 (78)	1.9×10^{-2}
2.85	6.55 (69)	3.9×10^{-2}
3.35	6.55 (66)	8.1×10^{-2}
3.65	6.55 (64)	1.4×10^{-1}
3.85	6.55 (63)	1.9×10^{-1}
4.34	6.55 (60)	> 1

[a](wt.%) = [silver(g) / (silver(g) − binder(g))] × 100%.

Table 3. Conductivity of the films prepared from silver flake/CAB 551-0.2 in MEK solution

CAB (g)	Silver flake [g [a](wt.%)]	Resistance (Ω/cm^2)
1.85	6.55 (78)	1.4×10^{-2}
2.85	6.55 (69)	3.2×10^{-2}
3.35	6.55 (66)	5.0×10^{-2}
3.65	6.55 (64)	7.2×10^{-2}
4.34	6.55 (60)	1.7×10^{-1}
4.74	6.55 (58)	3.4×10^{-1}
5.14	6.55 (56)	> 1

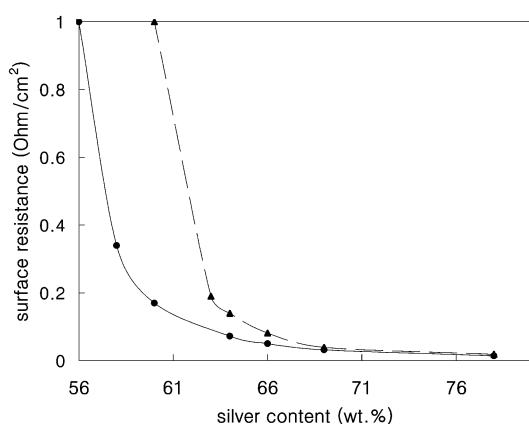[a](wt.%) = [silver(g) / (silver(g) − binder(g))] × 100%.

Fig. 1. Percolation curve of the conductivity for the CAB-based conductive paste containing the silver powder (dotted line) and silver flake (solid line).

nificant effect on the conductivity of the films prepared, and flake is superior to both particle and powder shapes.

Binder Type

In order to investigate the binder effects on the conductivity, silver flake was added to a MEK solution of various binders at different filler/binder ratios under the same conditions and the dried films, prepared in the same way as previously described, were monitored for their resistance. The results are sum-

marized in *Table* 4.

CAB 551-0.01 showed better conductivity (lower resistance) than the 551-0.2 and 381-0.1 versions and not much difference in conductivity was observed between CAB 551-0.2 and 381-0.1 over the ranges of filler/binder ratios. This indicates that the viscosity is an important factor which contributes to achieve an optimal silver flake configuration since the major difference between CAB 551-0.01 and the other CAB versions is their viscosity (*Table* 5).

It was thought that a binder with higher viscosity reduces the ability of the metal fillers to orient at the surface, and thus the optimal orientation of the fillers to generate the conductive path is impeded. To further investigate the viscosity effect, the sample with CAB 381-0.1 having the silver content of 56 wt.% was diluted from 50 wt.% to 40 wt.% and 33 wt.% of the total solid (CAB + silver) concentration, and their resistance was compared (*Table* 6).

Table 5. Physical data for various CABs used

CAB Type	M_n	viscosity	T_g (°C)	butyryl content [a](%)
551-0.2	30,000	0.2	101	52
381-0.1	20,000	0.1	123	37
551-0.01	16,000	0.01	85	53

[a](%) is the average value for the butyryl composition out of acetyl, butyryl and hydroxyl substituents in 1.

Table 4. Conductivity of the films prepared from silver flake with various types of binders in MEK solution. No additives were added and the concentration of the paste was set to 72.4 [b]wt.%.

	PBMA	P(BMA-*co*-MMA)	PMMA	CAB 551-0.2	CAB 381-0.1	CAB 551-0.01
Silver [a](wt.%)	Resistance (Ω/cm^2)	Resistance (Ω/cm^2)	Resistance (Ω/cm^2)	Resistance (Ω/cm^2)	Resistance (Ω/cm^2)	Resistance (Ω/cm^2)
78	Poor Film	Poor Film	Poor Film	1.4×10^{-2}	1.0×10^{-2}	Poor Film
69	9.5×10^{-2}	Poor Film	Poor Film	3.2×10^{-2}	2.4×10^{-2}	2.2×10^{-2}
66	1.6×10^{-1}	Poor Film	Poor Film	5.0×10^{-2}	4.7×10^{-2}	2.6×10^{-2}
64	2.9×10^{-1}	3.8×10^{-2}	3.1×10^{-2}	7.2×10^{-2}	6.0×10^{-2}	3.1×10^{-2}
60	> 1	6.5×10^{-2}	4.6×10^{-2}	1.7×10^{-1}	1.9×10^{-1}	4.1×10^{-2}
58		7.9×10^{-2}	4.8×10^{-2}	3.4×10^{-1}	4.0×10^{-1}	5.8×10^{-2}
56		1.1×10^{-1}	1.1×10^{-1}	> 1	> 1	7.8×10^{-2}
54		4.5×10^{-1}	2.2×10^{-1}			9.7×10^{-2}
52		> 1	> 1			1.7×10^{-1}
50						3.8×10^{-1}
48						> 1

[a](wt.%) = [silver(g) / (silver(g) + binder(g))] × 100%.

[b]wt.% = [(silver(g) + binder(g)) / (silver(g) + binder (g) + solvent(g)] × 100%.

Table 6. The dilution effect on the conductivity of the samples prepared with Ag/CAB 381-0.1 in MEK solution

CAB (g)	Silver [g [a](wt.%)]	[b]Concn (%)	Resistance (Ω/cm²)
2.56	3.27 (56)	50	> 10
2.56	3.27 (56)	40	1.3
2.56	3.27 (56)	33	3.4 × 10⁻¹

[a](wt.%) = [silver(g) / (silver(g) + binder(g))] × 100%.
[b]Concentration(%) = [(silver(g) + binder(g)) / (silver(g) + binder(g) + solvent(g))] × 100%.

As expected, better conductivity (lower resistance) was obtained as the sample was more diluted. As the viscosity of the solution is closely related to its concentration, this result confirmed that the viscosity is the key factor for determining the conductivity of the samples.

The CAB was then compared with other types of acrylic binders; PMMA, P(BMA-co-MMA) and PBMA (Table 5). The resistance for the Ag flake/PMMA system, having the lowest viscosity among three acrylic binders, was lower than that of Ag/P(BMA-co-MMA), which then revealed much lower resistance than that of Ag/PBMA, but the films obtained from both PMMA and P(BMA-co-MMA) were of worse quality. The films were in fact too poor to measure conductivity at the lower loading of these binders. Better films were formed as the loading of the PMMA or P(BMA-co-MMA) was increased. It was thought that PBMA and P(BMA-co-MMA) having more hydrophobic longer alkyl chains (butyl

group) better encapsulates the silver pigment, forming better coating, but this encapsulation of the pigment also caused higher resistance for the PBMA and P(BMA-co-MMA) system. Further studies involving various other acrylic binders having different molecular weights are, however, required for this assessment. The film's integrity also seemed to be adversely affected when the binder's loading was too low especially for the less viscous binder, such as PMMA. Interesting point from the results in Table 4 was that CAB 551-0.01 offered much better conductivity (lower resistance), together with lower percolation point than PMMA and P(BMA-co-MMA), two most widely used binders for the conductive ink system. In addition, all the CAB binders offered much better quality of the film than the acrylic binders even at low loadings. The better conductivity (lower resistance) of the film prepared using CAB was ascribed to its low viscosity, and the high butyl content in CAB (see Table 5) seemed to offer a good film-forming property. Considering the balance between conductivity and film quality, CAB 551-0.01 was regarded as the best binder among those investigated, and this was used for further studies. The studies, so far, have been mainly focused on the conductivity, and it was necessary to look into other properties such as flexibility.

Plasticizer

Plasticizer is a material of low molecular weight added to a polymer to separate the molecular chains.

Table 7. Plasticizer effect on the conductivity of the films prepared from silver flake/CAB-551-0.01 system. The concentration of the paste was 72.4 wt.%

CAB (g)	DBP (g)	Silver [g [a](wt.%)]	Resistance (Ω/cm²)	Resistance [b](Ω/cm²)
1.05	0.03	1.63 (60)	6.7 × 10⁻²	4.1 × 10⁻²
1.25	0.03	1.63 (56)	1.2 × 10⁻¹	7.8 × 10⁻²
1.47	0.03	1.63 (52)	3.3 × 10⁻¹	1.7 × 10⁻¹

CAB (g)	DBP (g)	Silver Content [g [a](wt.%)]	Resistance (Ω/cm²)	Resistance [b](Ω/cm²)
1.01	0.07	1.63 (60)	7.9 × 10⁻²	4.1× 10⁻²
1.21	0.07	1.63 (56)	1.7 × 10⁻¹	7.8 × 10⁻²
1.43	0.07	1.63 (52)	4.7 × 10⁻¹	1.7 × 10⁻¹

[a](wt.%) = [silver(g) / (silver(g) + binder(g) + DBP(g))] × 100%.
[b]Resistance value when no plasticizer was used at the same loadings of silver.

This results in a depression of the glass transition temperature, reduced stiffness and brittleness, and improved processability. Dibutyl phthalate (DBP) was used in 5 and 10 wt.% relative to CAB 551-0.01 and the resistance of the dried films at three filler/binder ratios (60/40, 56/44 and 52/48) was measured. As shown in *Table 7*, the resistance value for the samples containing the plasticizer was higher compared with their original silver/binder system, and the difference became larger as the silver/binder ratio gets closer to the percolation point.

When benzyl butyl phthalate was used as a plasticizer instead of dibutyl phthalate, much higher increase in resistance was observed. The preferred glass transition temperature of the binder for the conductive application is between 45 and 105 °C. Under 45 °C, blocking occurs, whereas films become fragile above 105 °C. The DSC studies for the samples containing CAB/dibutyl phthalate in 95/5 and 90/10 wt.% were attempted but did not give any reliable data. As the presence of the plasticizer seems to have an adverse effect on the conductivity, especially at the lower silver/binder ratio, the maximum loading of the plasticizer was set to 5 wt.% relative to the binder. The films containing this level of plasticizer appear to offer good flexibility. From the above results, it was found that the plasticizer not only provided benefits to the prepared films such as flexibility and uniformity, but they also adversely affected the conductivity of the Ag/CAB system. Therefore, it was concluded that the amount (and the type) of the plasticizer has to be carefully controlled.

Finally, it has to be added that the effect of the co-solvent was also investigated to control the drying rate using butyl acetate, and the results showed that the presence of the co-solvent significantly increased the resistance for the conductive paste. It was thought that the more viscous butyl acetate than MEK increased the overall viscosity of the solution, affecting its conductivity. The use of co-solvent was, therefore, not recommended as no significant improvement in the film's properties was obtained when the co-solvent was used.

Table 8. Conductivity for CAB-based conductive paste

Silver [a](wt.%)	Resistance (Ω/cm²)
69	5.2×10^{-5}
64	6.0×10^{-5}
60	6.7×10^{-5}
58	9.0×10^{-5}
56	1.2×10^{-1}
54	1.9×10^{-1}
52	3.3×10^{-1}
50	> 1

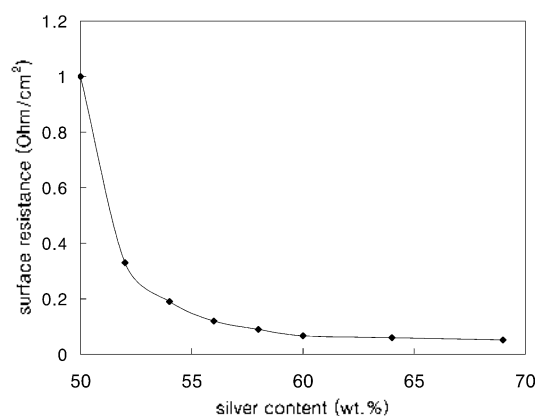[a](wt.%)=[silver(g)/(silver(g) + binder(g) + DBP(g))] · 100%.

Fig. 2. Percolation curve of the conductivity for the CAB-based conductive paste.

Developing CAB-based conductive paste

Based on the knowledge we have gained so far, the formulation for our conductive paste was suggested: silver flake as a metal filler, CAB 551-0.01 as a binder, dibutyl phthalate as a plasticizer and MEK as a solvent. The plasticizer/CAB ratio was 95/5 by weight and the total solid content [(silver(g) + CAB(g) + DBP(g)) / (silver(g) + CAB(g) + DBP(g) + MEK(g))] was 55 wt.%. The films prepared from this conductive paste showed surface resistance of 5.2×10^{-2} Ω/cm² and percolation point of 50 (*Table 8* and *Fig.* 2). A steep percolation curve and stable conductivity up to 60 wt.% of the silver loadings were obtained, implying that reliable conductivity can be produced regardless of the substrates applied onto and films' thickness. In addition, the films prepared from the CAB-based conductive paste offered uniform coating and good flexibility.

CONCLUSION

In summary, we have investigated the possibilities to use CAB as a binder for the conductive paste. Having both low viscosity and good metal-encapsulating properties hence good film-forming properties, CAB was concluded to be a good candidate as a binder for the conductive paste. We have also prepared a formulation for the conductive paste, which showed promising results. Finally, another very important factor to be considered for the choice of conductive paste is its drying rate: the current levels of conductivity, in fact, are suitable for the commercial application, but most of the conductive pastes dry too slowly at the thicknesses needed to allow for the higher speeds of printing. Therefore, a conductive paste which could deliver comparable conductivity with faster drying (and with lower cost, of course) could be the winner of all. This will be the focus of our future studies, together with the rheology of the conductive paste prepared.

REFERENCES

1. Gentile, C.; Wallace, M.; Avalon, T.; Goodman, S.; Fuller, R.; Oaks, S.; Hall, T. US Patent 5,086,785 (1992).
2. Jurgens, J.; Patterson, P. *Med. Eng. Phys.* **1997**, *19*, 1.
3. Young, C. R.; Koleng, J. J.; McGinity, J. W. *Int. J. Pharma.* **2002**, *242*, 87.
4. Gilbert, R. D.; Venditti, R. A.; Zhang, C.; Koelling, K. W. *J. Appl. Polym. Sci.* **2000**, *77*, 418.
5. Qiu, W.; Zhang, F.; Endo, T.; Hirotsu, T. *J. Appl. Polym. Sci.* **2003**, *87*, 337.
6. Choi, S. H.; Cho, M. S.; Kim, D.; Kim, J.-H.; Lee, D. H.; Shim, S. J.; Nam, J.-D.; Lee, Y. *Polymer(korea)*, **2005**, *29*, 399.
7. Kosaka, P. M.; Kawano, Y.; Salvadori, M. C.; Petri, D. F. S. *Cellulose*, **2005**, *12*, 351.
8. Higashi, F.; Cho, C. S.; Kakinoki, H.; Sumita, O. *J. Polym. Sci. Polym. Chem. Ed.* **1977**, *15*, 2303.
9. Buckley, M. S.; Bowns, R. E. US Patent 5,286,415 (1994).
10. It was also found that the conductivity of the silver flake/CAB samples was slightly increased with the addition of zinc stearate (ZS) as an additive, but this improvement in conductivity was not observed for the silver powder/CAB/ZS system. It was thought that zinc stearate acted as a leafing agent to bring the silver flake to the surface area, but this was not effective for the silver powder.