

Preparation and rheological behavior of lead-free graphite conducting paste

Luo Shiyong, Xu Wencai, Wang Ning,
Chen Meng, Lv Yong

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Abstract A lead-free graphite conducting paste was prepared by using graphite powder, lead-free barium boron low-melting glass and ethyl cellulose solution. By analyzing the sheet resistance, Vickers hardness as well as the adhesion strength of the fired film prepared by the pastes formulated with different composition, the composition of the paste with preferable properties was evaluated in weight percent: organic vehicle 60, graphite powder 15–20, and low-melting glass 20–25. The films, prepared by the pastes using the lead-free glass with a glass transition temperature of 476°C, were perfectly flat and compact after fired at a peak temperature within the range of 540 to 590°C. The sheet resistance of the fired film with glass content of 25 wt% was 135 Ω/mm^2 at the film thickness of $25 \pm 3 \mu\text{m}$, while the Vickers hardness was 12.3 N/mm^2 and the adhesion strength to soda lime silicate glass substrate was 45.6 N/mm^2 . In addition, the rheological, thixotropic, and viscoelasticity behaviors of the typical paste were characterized and the effects on the screen-printing ability were analyzed in detail. It is found that a slight flocculated network structure is formed in the paste at rest, but the flocculated structure is very slight due to the steric effect of the ethyl cellulose macromolecules and good dispersing. The rheological, thixotropic, and viscoelasticity behaviors of the typical paste were similar to those of the screen-printing pastes with a high solid content of filler.

Keywords Graphite conducting paste, Thick film, Rheological behavior, Lead free

Introduction

Graphite thick films are used extensively for versatile thick film electrodes,^{1–4} anti-electrostatic coatings,⁵ etc. Graphite conducting thick film paste consists of primarily three functional constituents: (1) the graphite powder, which provides the conductive phase; (2) low-melting glasses, which act as a permanent binder during sintering to enable binding of the functional graphite powder to the substrate; and (3) organic vehicle, which disperses the graphite powder and low-melting glass powder to impart the desired rheological properties to the paste. The paste is screen-printed in the desired pattern onto the substrate, dried, and fired at high temperatures in order to realize conducting films with a thickness ranging from 10 to 30 μm . However, the mainly used low-melting glasses as the permanent binder in thick film pastes are lead borosilicate glass with PbO typically more than 70 wt%.^{6,7} Recently, lead contained low-melting glass in thick films has been restricted because it is dangerous to health and environment. This tendency leads to efforts in the direction of the development of lead-free low-melting glass binder. Generally, the firing temperature of lead-free low-melting glasses is higher than that of lead-contained glasses. Thus, it is very important to use new lead-free low-melting glass to alternate lead-contained low-melting glass for the lead free of electric components.

In this investigation, lead-free graphite conducting pastes were prepared by using graphite powder as conducting phase, a lead-free barium boron glass as permanent binder, and ethyl cellulose solution as organic vehicle. The effects of glass frit content on the sheet resistance, Vickers hardness, as well as the

L. Shiyong (✉), X. Wencai, C. Meng, L. Yong
The Laboratory of Printing & Packaging Material and
Technology, Beijing Area Major Laboratory, Beijing
Institute of Graphic Communication, Beijing 102600,
People's Republic of China
e-mail: luoshiyong@bigc.edu.cn

W. Ning
The Laboratory for Study of Earth's Interior and Geo
Fluids, Institute of Geochemistry, Chinese Academy of
Sciences, Guiyang 550002, People's Republic of China

adhesion strength of the fired film to the soda lime silicate glass substrate were investigated. The rheological, thixotropic, and viscoelasticity behaviors of the typical paste were characterized by using a rheometer and the effects on the screen-printing ability were analyzed in detail.

Experimental

Commercially available graphite powder was used as conducting phase. The average particle size of flake graphite powder was 0.4 μm . Figure 1 shows the X-ray diffraction pattern of the graphite powder (Rigaku, D/MAX 2200). One sees that the diffractogram is very close to the characteristic peaks of crystalline graphite-2H, given by JCPDS file no. P63/mmc(194).

A lead-free barium boron glass was used as permanent binder. The glass was melted at 1050°C and then fritted, pulverized to an average particle size of about 3 μm . Table 1 shows the detailed composition and properties of the glass. The glass transition temperature of the glass was 476°C, which was determined by the quantitative differential thermal analyzer of DSC-200PC.

The organic vehicle was a solution prepared by solving 4 wt% ethyl cellulose and some additives in the mixing solvents of butylcarbitol acetate and terpineol. The *N*-type ethyl cellulose was used. The substitution number of ethoxy for the hydroxy in each glucose unit

of the *N*-type ethyl cellulose was 2.4–2.5; correspondingly, the weight percent of the ethoxy is 47–48.

The thick film pastes were formulated having the composition of graphite powder, barium boron glass powder, and the organic vehicle. Table 2 gives the different paste compositions having varying weight percentages of glass content with constant inorganic-to-organic ratio of 40:60. The above materials were admixed thoroughly and then ground to the required consistency in a three-roll mixer.

The rheological and thixotropic behaviors of the formulated pastes were analyzed by an ARES(RFS-III) rheometer. For all measurements the geometry was limited to cone and plate; a titanium cone-and-plate geometry with a radius of 25 mm and a cone angle of 0.04 radian was used. Dynamic frequency sweep tests were carried out with a controlled strain of 5%. The experiments were carried out in an environment with controlled relative humidity, and the measurement temperature was 20°C.

The formulated pastes were screen-printed through a nylon mesh (mesh count 250) on 100 x 100 mm soda lime silicate glass substrate. The screen-printed samples were then dried at 180°C for 10 min, and then fired in the high-temperature muffle furnace at 540, 550, 560, 570, 580, and 590°C peak temperature for 10 min, respectively. The resultant fired film samples were analyzed for surface morphology, thickness, Vickers hardness, and adhesion strength by an SS550 scanning electron microscopy (SEM), FTS-S3C surface profile meter, HXS-1000 digital intelligent microscopy sclerometer, and WS-2002 Scratch Tester for adhesion strength of film to substrate by scratching film, respectively. The sheet resistance of the fired films was measured using the four-point technique.

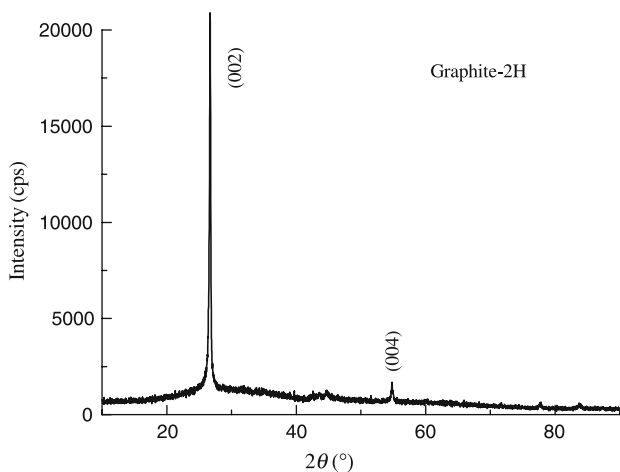


Fig. 1: The XRD pattern of the graphite powder

Table 2: Composition of the graphite conducting pastes prepared (wt%)

Sample number	Graphite powder	Glass powder	Organic vehicle
S1	35.00	5.00	60.00
S2	30.00	10.00	60.00
S3	25.00	15.00	60.00
S4	20.00	20.00	60.00
S5	15.00	25.00	60.00
S6	10.00	30.00	60.00
S7	5.00	35.00	60.00

Table 1: The composition and properties of the glass used in the paste

Component	SiO ₂	B ₂ O ₃	BaO	Bi ₂ O ₃	Al ₂ O ₃	ZnO	SnO ₂
Content (mol%)	2	15	47	23	2	8	3
Density (g/cm ³)						2.8	
Glass transition temperature (°C)						476	

Table 3: Hardness, sheet resistance, and adhesion strength of the fired films prepared by the graphite conducting pastes

Sample number:	S1	S2	S3	S4	S5	S6	S7
Adhesion strength (N/mm ²)	×	×	×	24.1	45.6	79.9	123.8
Vickers hardness (N/mm ²)	–	–	–	8.7	12.3	15.4	22.9
Sheet resistance (Ω/mm ²)	–	–	–	80	135	∞	∞

Note: “×” represents that the graphite powder in the sintered film is ease to come off. “–” means that the Vickers hardness and sheet resistance were not tested

Results and discussion

Glass content in the graphite conducting paste

The film samples after screen printed and then fired at 540, 550, 560, 570, 580, and 590°C peak temperature for 10 min, respectively, were analyzed. Table 3 shows the hardness, sheet resistance, and adhesion strength of the films prepared by the graphite conducting pastes with the composition formula given in Table 2. The thickness of the film was about $25 \pm 3 \mu\text{m}$, which was determined by FTS-S3C surface profile meter. The surface morphology of the fired thick films was observed by an SS550 model SEM. The graphite powders in the film surface of the samples S1, S2, and S3, with the glass content less than 15 wt% in the paste, were ease to come off, while the film samples S6 and S7, with the glass content more than 30 wt%, were insulating. However, the sheet resistance of the film samples S4 and S5, with the glass weight content of 20 and 25%, was 80 and 135 Ω/mm², respectively. The film sample S5 was prepared by screen-printing the paste sample no. S5 in Table 2 on soda lime silicate glass substrate, then fired at 590°C peak temperature for 10 min. It was perfectly flat and compact. Figure 2

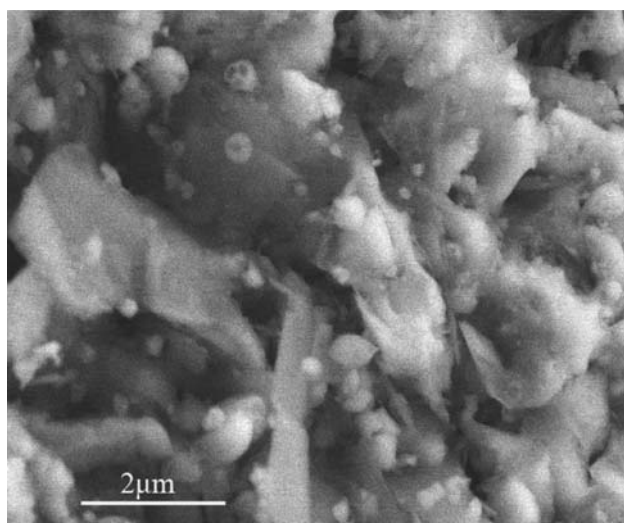


Fig. 2: SEM photograph of the fired thick film, prepared by screen-printing the paste sample no. S5 in Table 2 on soda lime silicate glass substrate, then fired at 590°C peak temperature for 10 min

gives a SEM micrograph of the fired film S5. As expected, the sheet resistance, Vickers hardness, and adhesion strength of the film samples increase with an increase of the glass content.

It is seen that glass weight percentage of 20–25, corresponding to sheet resistance of about 80–135 Ω/mm², would be suitable for the conductor composition. A glass weight percentage of 20–25 is found to be ideal for the present thick film conducting paste formulation, which beneficially offers favorable microstructure, hardness, good adhesion strength, and desired low sheet resistance in the film after firing. The film prepared by the paste of no. S5 in Table 2, with the glass content of 25 wt%, was smooth and compact. Its sheet resistance was 135 Ω/mm², the Vickers hardness was 12.3 N/mm², and the adhesion strength to soda lime silicate glass substrate was 45.6 N/mm².

Rheological behavior

Rheological characterization of a paste is to measure the relationship between shear stress and rate of shear strain varying harmonically with time, indicating the level of interparticle force or flocculation in the paste.⁸ The time-dependent rheology of the paste sample no. S5 in Table 2 was characterized directly using ARES rheometer. Figure 3 presents the result. The paste has

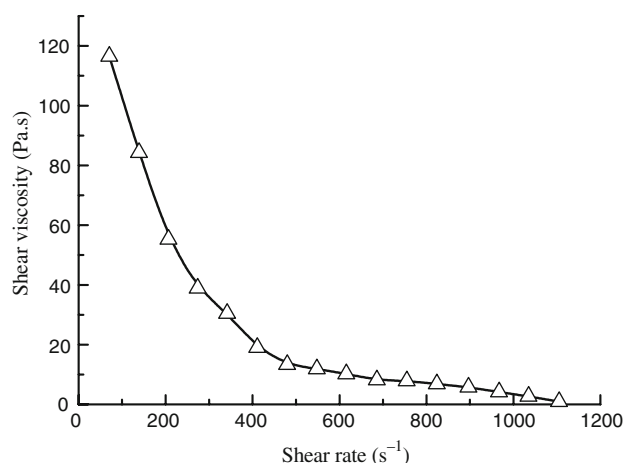


Fig. 3: Shear viscosity versus shear rate curve of the paste sample no. S5 shown in Table 2

a typical rheological behavior of pseudoplastic fluid. The apparent viscosity decreased rapidly with the increase of the shear rate. The paste would flow as long as the imposed stress exceeds a specific threshold. This threshold is known as the yield stress. The stress exceeding the threshold will be reduced as the strain rate increases, because entanglement between ethyl cellulose macromolecules in the paste is released subject to the stress, which results in decreasing of viscosity. The apparent viscosity of polymer will decrease as the shear rate increases. This can be attributed to the polymer chain pulled apart to be arranged in straight chain when the polymer is in shear flows. If the shear rate increases, the viscosity will decrease accordingly. The particles in the paste were flocculated slightly when the paste was at rest and de-flocculated under shear. The shear thinning rheological behavior was desired for the screen-printing and to avoid sedimentation in store.

The screen-printing process can be divided into the following steps: pastes printed on the substrate plate through the opening of the screen mesh, snap off due to the screen mesh gradually separating from the substrate plate by the screen tension, and paste surface leveling after removal of the screen plate. When the paste is penetrating the opening of the screen mesh, it is subjected to the maximum shear rate.⁹ Hence, the shear viscosity at high shear rate is very important for the printing ability of the paste. Lin et al.⁹ had discussed the relationship between the printing ability of various pastes and the shear viscosity of the paste at high shear rate. They conclude that if the paste has excessively high viscosity at a shear rate up to 1000 s^{-1} , leading to uneasy through printing, difficult snap off, or even adhesion, while the viscosity is extremely low at high shear rate, resulting in smudging, and when the viscosity values at a high shear rate of 1000 s^{-1} lie between 1.0 and 2.5 Pa·s, the pastes have the best printing quality. Though the shear viscosity of the paste sample no. S5 shown in Table 2 is about 3 Pa·s, the paste has good screen-printing ability and printing quality.

Thixotropic behavior

Thixotropy of paste materials has often been quantified by measuring the surface of what is called the “thixotropic loop” or at least a surface linked to this thixotropic loop.^{10–12} The stress/shear rate curve of the paste sample no. S5 in Table 2 was measured successively using ARES rheometer during increasing and decreasing sequences of applied shear rates. The test result is given in Fig. 4; during the increasing shear rate ramp, de-flocculation occurs but not quickly enough to reach the steady state shear stress. The measured stress is thus always higher than what would be obtained if steady state was reached. On the other hand, during the decreasing shear rate ramp, flocculation occurs but here again not quickly enough for

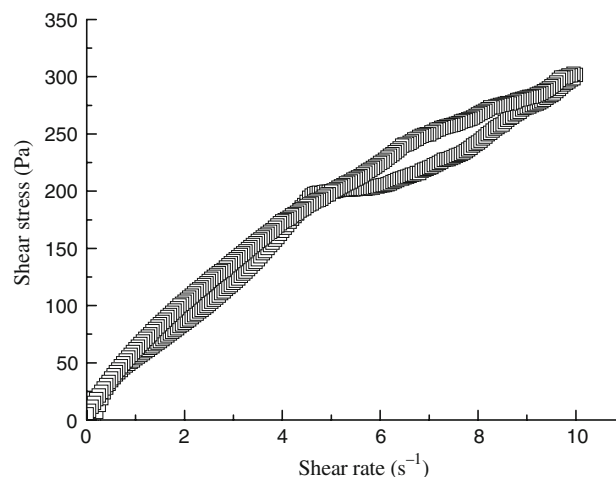


Fig. 4: Thixotropic loop obtained with the paste sample no. S5 shown in Table 2 submitted successively to increasing and decreasing shear rate ramps

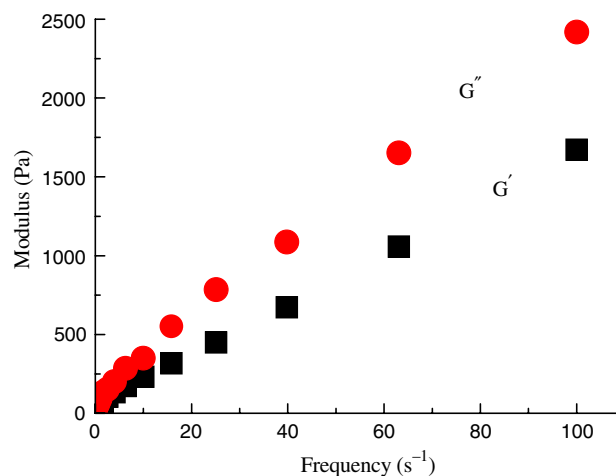


Fig. 5: The viscoelasticity of the paste sample no. S5 shown in Table 2

steady state to be reached and the measured stress stays lower than steady state. The surface area between the two curves is measured and considered as representative of the work done per unit time and unit volume of the paste to break some of the initially present flocculation. Slightly flocculated dispersions are often thixotropic.⁸ It has been noted that the particles in the paste have flocculated at rest, but the flocculation is very slight since the surface area of the “thixotropic loop” is small.

Viscoelastic behavior

Figure 5 illustrates the frequency dependence of storage modulus (G') and loss modulus (G'') of the paste sample no. S5 in Table 2. For a viscoelastic material,

the storage modulus G' is taken as a measure of the energy stored in the materials and recovered from it per cycle, and is dependent upon what rearrangements can take place within the period of oscillation, which is used to estimate the elastic behaviors of the materials. On the other hand, the loss modulus G'' measures the energy dissipated or lost per cycle of sinusoidal deformation, and it is characteristic of the viscous behaviors.^{13,14} It shows that the storage modulus (G') and loss modulus (G'') are strongly dependent on the frequency. Both the values of G' and G'' increased with the increasing frequency. G'' is higher than G' at all frequency range, indicating that the paste exhibits liquid-like behaviors, i.e., its viscosity.¹⁵ This behavior is an indication of a viscous solution performance. It has been suggested in the literature¹⁵⁻¹⁸ that there is the same behavior where the values of the G'' are more than those of the G' in the pastes of the nano-sized solid powders dispersed in organic vehicle. Generally, the flow ability of the pastes with micron-sized powder fillers is better than that of the pastes with nano-sized powder fillers. In the present investigation, the fillers were micron-sized powder, and the disperse agent was added in the paste. Moreover, the paste was ground to the consistency $<15\ \mu\text{m}$ in a three-roll mixer. The powder fillers in the present paste were well dispersed. So, the paste exhibited a viscous property. However, shear-thinning behavior and the observation of a yield stress indicate the presence of a slight elastic network structure in the paste. In addition, the thixotropic behavior of the paste had demonstrated that the particles in the paste had flocculated slightly at rest. Thus, it can be concluded that a slight flocculated network structure had formed in the paste with a high solid content of filler, but the flocculated structure is very slight due to the steric effect of the ethyl cellulose macromolecules and good dispersing.

Conclusion

The lead-free graphite conducting pastes were prepared by using graphite powder, lead-free barium boron low-melting glass, and ethyl cellulose solution. A glass weight percentage of 20–25 is found to be ideal for the present thick film conducting paste formulation, which beneficially offers favorable microstructure, hardness, good adhesion strength, and desired low sheet resistance in the film after firing. The film prepared by the paste with the glass content of 25 wt% was smooth and less pin-holes microstructure. Its sheet resistance was $135\ \Omega/\text{mm}^2$, the Vickers hardness was $12.3\ \text{N}/\text{mm}^2$, and the adhesion strength to soda lime silicate glass substrate was $45.6\ \text{N}/\text{mm}^2$. It is found that a slight flocculated network structure is formed in the paste at rest, but the flocculated structure is very slight due to the steric effect of the ethyl cellulose macromolecules and good dispersing. The rheological, thixotropic, and viscoelasticity behaviors

of the typical paste were similar to those of the screen-printing pastes with a high solid content of filler. The paste is applicable for manufacturing electrical components on soda lime silicate glass substrate since the favorable fired temperature range of the paste was from 540 to 590°C.

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References

1. Cao, L, Jia, J, Wang, Z, "Sensitive Determination of Cd and Pb by Differential Pulse Stripping Voltammetry with In Situ Bismuth-Modified Zeolite Doped Carbon Paste Electrodes." *Electrochim. Acta*, **1** (53) 2177–2182 (2008). doi:10.1016/j.electacta.2007.09.024
2. Aramoto, T, Adurodija, F, Nishiyama, Y, Arita, T, Hanafusa, A, Omura, K, "A New Technique for Large-Area Thin Film CdS/CdTe Solar Cells." *Sol. Energy Mater. Sol. Cells*, **75** 211–217 (2003). doi:10.1016/S0927-0248(02)00161-7
3. Ibrahim, H, "Carbon Paste Electrode Modified with Silver Thimerosal for the Potentiometric Flow Injection Analysis of Silver(I)." *Anal. Chim. Acta*, **545** 158–165 (2005). doi:10.1016/j.aca.2005.04.083
4. Guo, H, He, N, Ge, S, Yang, D, Zhang, J, "Molecular Sieves Materials Modified Carbon Paste Electrodes for the Determination of Cardiac Troponin I by Anodic Stripping Voltammetry." *Microporous Mesoporous Mater.*, **85** 89–95 (2005). doi:10.1016/j.micromeso.2005.06.022
5. Do, CH, Kwasngyun, C, Seung, H, "Electromagnetic and Electromagnetic Wave Absorbing Properties of the Epoxy-Carbon Black Composite." *Polym-Korea*, **21** (1) 119–124 (1997)
6. Morena, R, "Phosphate Glasses as Alternatives to Pb-Based Sealing Frits." *J. Non-Cryst. Solids*, **263–264** 382–387 (2000)
7. Ketkar, SA, Umarji, GG, Phatak, GJ, Ambekar, JD, Rao, IC, Mulik, UP, Amalnerkar, DP, "Lead-Free Photoimageable Silver Conductor Paste Formulation for High Density Electronic Packaging." *Mater. Sci. Eng. B*, **132** 215–221 (2006). doi:10.1016/j.mseb.2006.02.027
8. Roussel, N, "A Thixotropy Model for Fresh Fluid Concretes: Theory, Validation and Applications." *Cem. Concr. Res.*, **36** 1797–1806 (2006). doi:10.1016/j.cemconres.2006.05.025
9. Lin, H-W, Chang, C-P, Hwu, W-H, Ger, M-D, "The Rheological Behaviors of Screen-Printing Pastes." *J. Mater. Sci. Technol.*, **197** 284–291 (2008)
10. Lapasin, R, Longo, V, Rajgelj, S, "Thixotropic Behaviour of Cement Pastes." *Cem. Concr. Res.*, **9** 309–318 (1979). doi:10.1016/0008-8846(79)90123-6
11. Lapasin, R, Papo, A, Rajgelj, S, "Flow Behaviour of Cement Pastes. A Comparison of Different Rheological Instruments and Techniques." *Cem. Concr. Res.*, **13** 349–356 (1983). doi:10.1016/0008-8846(83)90034-0

12. Assaad, J, Khayat, K, Mesbah, H, "Assessment of Thixotropy of Flowable and Self-Consolidating Concrete." *ACI Mater. J.*, **100** (2) 99–107 (2003)
13. Boutelier, D, Schrank, C, Cruden, A, "Power-Law Viscous Materials for Analogue Experiments: New Data on the Rheology of Highly-Filled Silicone Polymers." *J. Struct. Geol.*, **30** 341–353 (2008). doi:[10.1016/j.jsg.2007.10.009](https://doi.org/10.1016/j.jsg.2007.10.009)
14. Nasser, MS, James, AE, "Compressive and Shear Properties of Flocculated Kaolinite–Polyacrylamide Suspensions." *Colloids Surf. A*, **317** 211–221 (2008). doi:[10.1016/j.colsurfa.2007.10.021](https://doi.org/10.1016/j.colsurfa.2007.10.021)
15. Wei, H, Zhang, Y, Xu, J, "The Dynamic Rheology Behaviors of Reactive Polyacrylic Acid/Nano-Fe₃O₄ Ethanol Suspension." *Colloids Surf. A*, **296** 51–56 (2007). doi:[10.1016/j.colsurfa.2006.09.021](https://doi.org/10.1016/j.colsurfa.2006.09.021)
16. Tatsumi, D, Kouroggi, H, Chen, B, Matsumoto, T, "Effect of Natural Additives on the Rheological Properties of Cellulose Fiber Disperse Systems." *Colloids Surf. A*, **316** 151–158 (2008). doi:[10.1016/j.colsurfa.2007.09.001](https://doi.org/10.1016/j.colsurfa.2007.09.001)
17. Choi, CS, Park, BJ, Choi, HJ, "Electrical and Rheological Characteristics of Poly(Vinyl Acetate)/Multi-Walled Carbon Nanotube Nanocomposites." *Diamond Relat. Mater.*, **16** 1170–1173 (2007). doi:[10.1016/j.diamond.2006.11.075](https://doi.org/10.1016/j.diamond.2006.11.075)
18. Park, S-D, Han, D-H, Teng, D, Kwon, Y, "Rheological Properties and Dispersion of Multi-Walled Carbon Nanotube (MWCNT) in Polystyrene Matrix." *Curr. Appl. Phys.*, **8** 482–485 (2008). doi:[10.1016/j.cap.2007.10.062](https://doi.org/10.1016/j.cap.2007.10.062)