

A Rheological Study of a Textile Coating Paste Containing PEDOT:PSS

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ABSTRACT

A conductive coating paste suitable for knife coating of textiles can be obtained with PEDOT:PSS, a polyurethane based binder, ethylene glycol and a rheology modifier. The influence of each component, as well as combinatory effects, has been studied with shear viscometry. Indicated associative interactions between the components are discussed.

INTRODUCTION

Textiles with improved electrical conductivity have been used for a long time in order to come around the hazards of electrostatic discharge (ESD). In the quest for “smarter” textiles, much higher conductivity than that required for ESD or antistatic applications are now needed. Electromagnetic interference (EMI) shielding, fabric circuits, heating and textile sensors¹ are applications commonly mentioned and, true enough, are becoming a reality due to new and better emerging technologies.

Within the area of conductive textile coatings, metallization by plating or sputtering are common routes of achieving textiles with high surface conductivity. An alternative route is using polymerization of conducting polymers, such as polypyrrole,

onto the textile². Aqueous dispersions of conducting polymers such as poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS) are now becoming increasingly available. It therefore seems more straightforward to simply add this ingredient to a traditional textile coating paste suitable for the industrially common process of knife coating.

In knife coating, the viscosity of the coating paste at high shear rates influences the rate at which the paste can be spread onto the textile whilst the viscosity at low shear rates influences the film formation³. Coatings should penetrate deep enough to give a good adhesion to the textile substrate although too deep penetration may cause the paste to bleed through. A good coating paste should therefore have a low viscosity at high shear rates and a high viscosity at low shear rates³. This is most commonly accomplished by adding a thickener of some sort, such as hydroxyethylcellulose (HEC) or a hydrophobically modified ethoxylated polyurethane (HEUR)⁴. To our knowledge, no study has yet been performed regarding thickening of a polyurethane-based coating pastes containing PEDOT:PSS and EG using a HEUR-type thickener.

EXPERIMENTAL

Materials

The binder paste was Performax 16297 G (Diazo AB, Sweden), a water dispersion of thermoplastic polyesterbased polyurethane, thickened with a hydrophilic thickener. Further details regarding the binder have been excluded as requested by the supplier. The PEDOT:PSS was Clevios PH1000 (Heraeus GmbH, Germany, denoted *Cle*), a water dispersion with 1.3 wt% solids content according to the manufacturer which was confirmed by drying. The ethylene glycol (denoted *EG*) was supplied by Sigma-Aldrich. The EG had a boiling point of 198°C and a room temperature viscosity of 21 mPas. The thickener was Borch Gel L75N (Borchers GmbH, Germany, denoted *HEUR*)

Mixing

Samples were prepared by batchwise mixing at 400 rpm for 3 min in a 250 ml glass beaker using a pitched-blade stirrer with a diameter of 60 mm. The inclination of the pitch blades was 10° to the horizontal plane. Each batch was between 60 and 100 g.

Viscosity measurements

The steady state shear viscosity was measured at 27°C with a cone-and-plate setup on a stress-controlled rheometer (Bohlin CS Melt, Sweden). Silicone oil was applied to the sample in order to stop skin formation during measurement. The integration time was 200 s at the lowest shear stress, gradually decreasing with increasing shear stress. Measurements went from high to low and then up to high shear stresses again. The stress sweep range was between 2 and 140 Pa.

RESULTS

The effect of adding various amounts of *Cle*, water or *EG* on the rheological properties of the paste can be seen in Fig. 1.

Not surprisingly, a diluting effect is seen in all cases, increasing amounts of each additive lead to a corresponding decrease in viscosity. Increasing amounts of additive also lead to a decreasing hysteresis effect (less thixotropy).

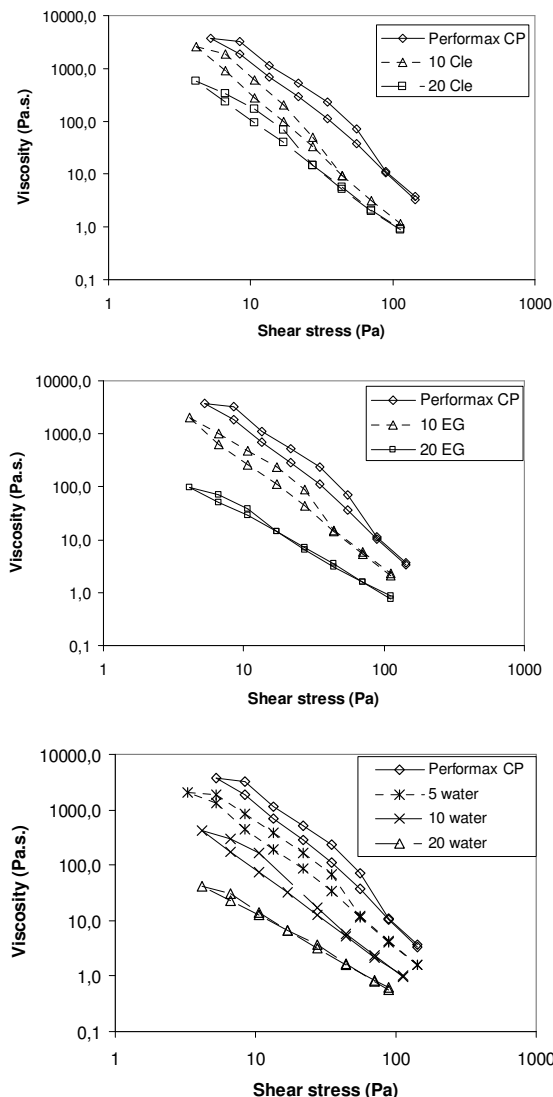


Figure 1. Viscosity vs shear stress for different amounts of additives, measured with a cone-and-plate setup. *Cle* denotes the PEDOT:PSS dispersion and *EG* denotes the ethylene glycol. The binding paste was measured with a cone-and-plate setup (Performax CP).

The difference between each additive when 20 parts were added can be seen in Fig. 2. At low shear stresses, water had the most diluting effect, followed by EG and then Cle. At high shear stresses, the difference between EG and Cle has vanished, whilst the difference between water and Cle remains. The combination of 10 parts Cle and 10 parts EG falls right between the two curves showing a lack of combinatory effects on the viscosity, although a notably high hysteresis effect at low shear stresses can be seen. 20 parts Cle showed a significantly higher hysteresis effect compared with 20 parts of EG or water.

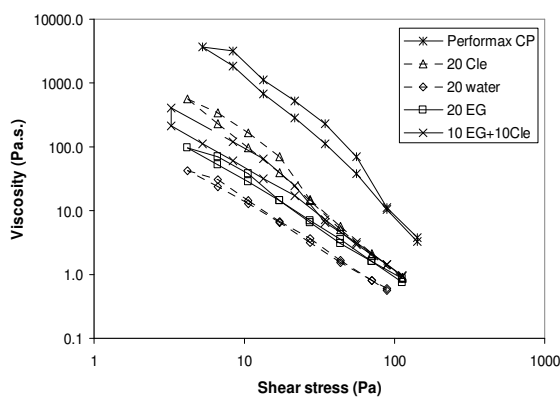


Figure 2. Viscosity vs. shear stress for a total addition of 20 parts of water, Cle or EG. The combination 10 parts EG + 10 parts Cle shows a lack of combinatory effects. At high shear stresses, 20 EG and 20 Cle as well as the 10 EG + 10 Cle combination shows more or less identical values. At low shear stresses, there is a significant difference.

It is interesting to note that the slope in the viscosity curves seems to change below a certain shear stress and that this change is more pronounced when Cle is added. If we assume that the PEDOT:PSS can be viewed as swollen gel particles and that these gel particles occupy a significant space in the polyurethane dispersion, then the influence at low shear stresses would only come from

the liquid which is not part of the gel particles. A fair correlation at low shear stresses was seen between 5 parts of water and 10 parts of Cle as well as between 10 parts of water and 20 parts of Cle, shown in Fig. 3. This means that PEDOT:PSS gel particles form a part of the network of gel particles. With increasing shear stress, the network of gel particles is destroyed more rapidly in the case of Cle, indicating that the interactions are somewhat weak.

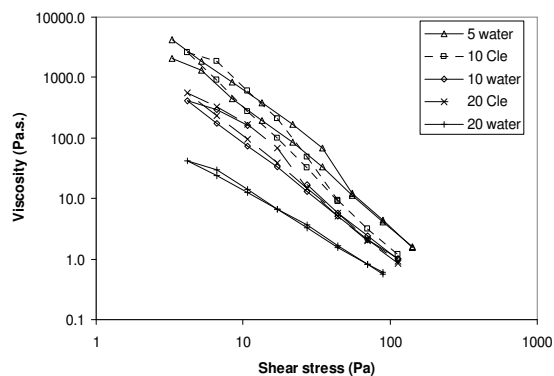
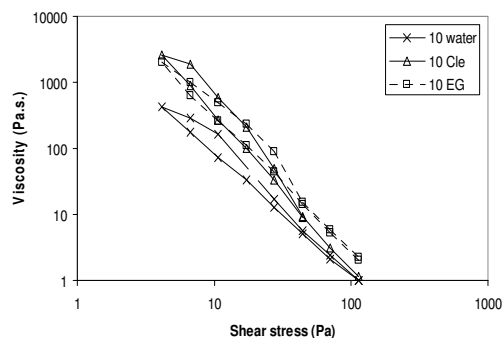
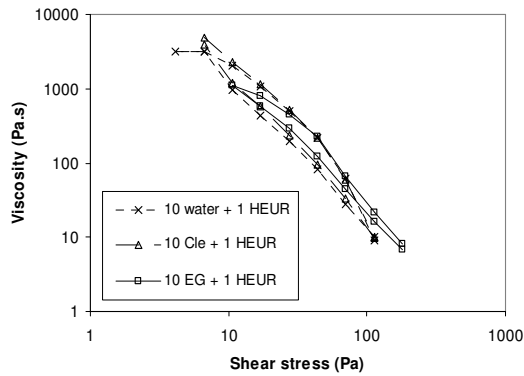


Figure 3. Shear viscosity vs. shear stress of pastes with 5, 10 or 20 parts of water and CP added. Assuming 50% of the volume is occupied by gel particles, fair correlation at low shear stresses can be seen, especially when comparing 10 water with 20 Cle.

When 1 part of HEUR was added to the paste, its effect on the viscosity was dominating yielding almost identical curves for 10 parts water and Cle, as seen in Fig. 4. However, the EG did not follow the same behaviour and a significant difference in the slope of the viscosity curve can be seen.



a)



b)

Figure 4. Viscosity vs. shear stress shown for diluted samples (a) and with 1 part of HEUR thickener added (b). Water and Cle show almost identical curves after the thickener has been added whilst EG shows significantly less thixotropy as well as less shear thinning.

DISCUSSION

Surface conductivities in the order of 100-1000 Ohms/sq have been achieved using the additives studied in this paper, although with different amounts. In this paper however, only the influence of the additives on the rheological behaviour of the paste is discussed, any discussion regarding their influence on conductivity is omitted and will be discussed in a future paper.

A decreasing hysteresis effect was seen in all cases with increasing amount of additive, see Fig. 1. The hysteresis effect can be related to the formation of an unstable network which is broken at high shear stresses and reforms at low shear stresses⁵, i.e. thixotropy. Additives are therefore likely to reduce the stiffness of the network (leading to decreasing viscosity) by increasing the distance between gel particles⁶. Addition of EG seemed to change the slope towards a less steep curve (Fig. 4). This indicates that the stiffness of the network which binds the polymer has been affected by the ethylene glycol in an unfavourable way. Reducing the amount of EG in the paste would therefore be useful in

order to get a paste with good processing properties, that is a paste with low viscosity at high shear rates and high viscosity at low shear rates. The effect EG has on the conductivity of the coating paste will be disclosed in a future paper. It is quite possible that excess EG in the coating influences not only the rheological behaviour but also factors such as the peel strength of the coating, more experimental work would be needed to clarify this.

It is interesting to see the similarities of adding water and Cle to the coating paste, especially after the thickener is added (Fig. 4). This indicates that there is good compatibility between the water dispersion, the binder and the thickener. It is possible that other thickeners may have a similar effect on the viscosity, for example alkali swellable acrylic emulsions (ASE). These thickeners operate using electrostatic repulsion of polymer chains causing them to swell⁴. In order to create this repulsion, the pH of the paste must be raised which would influence the conductivity of the PEDOT:PSS. The influence on viscosity and conductivity of adding this type of thickener to the binder would require further experiments.

CONCLUSIONS

Adding PEDOT:PSS as a water dispersion to a thermoplastic polyesterbased polyurethane water dispersion had a diluting effect on the viscosity. Adding ethylene glycol also had a diluting effect on the viscosity, but also altered the rheological profile towards a less shear thinning behaviour.

The HEUR-type thickener Borchi Gel L75N showed good compatibility with the PEDOT:PSS water dispersion and was suitable for thickening the paste.

ACKNOWLEDGEMENTS

The financial support from Vinnova through the Smart Textiles Technology Lab is gratefully acknowledged. Prof. Pernilla Walkenström from Swerea IVF and Prof. Bengt Hagström, also from Swerea IVF, are thanked for their scientific guidance.

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