J Mater Sci (2009) 44:2736–2742
DOI 10.1007/s10853-009-3357-3

Influence of polyvinylpyrrolidone on properties of flexible electrically conducting indium tin oxide nanoparticle coatings

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Received: 1 January 2009 / Accepted: 17 February 2009 / Published online: 9 March 2009

Abstract The influence of the organic film agent polyvinylpyrrolidone (PVP) on the electrical conductivity of indium tin oxide (ITO) nanoparticle coatings on polyethyleneterephthalate films was investigated. The ITO/PVP nanocomposite coatings show a decrease of the specific resistance with increasing PVP content up to 40 vol.%, whereas for higher PVP contents the specific resistance increases. The lowest specific resistance of 6 Ω cm is almost 20 times lower than that of a pure ITO nanoparticle coating. Annealing at 200 °C leads to a further decrease of the specific resistance for all volume fractions of PVP. Specific resistances of 0.5 Ω cm could be achieved for PVP contents of 33–40 vol.%. In addition, the PVP has a strong influence on the electrical conductivity of ITO/PVP coatings under bending which was investigated using a specially constructed device for the application of various bending loads. The ITO/PVP nanocomposite films show a significant lower increase of the sheet resistance under oscillatory bending compared to pure ITO nanoparticle coatings. However, the transmission in the visible range of ITO/PVP nanocomposites decreases with increasing PVP content up to 40 vol.%.

Introduction

Indium tin oxide (ITO) coatings are essential for many applications in different technological fields as, e.g., antireflection films, antistatic and antiglare shielding and transparent electrodes in displays. Classically, ITO is deposited on glass or polymer substrates by PVD techniques such as magnetron sputtering [1] or evaporation [2]. However, these techniques are costly due to the vacuum process necessary and the additional structuring process which causes some wastage of ITO. The use of ITO nanoparticle dispersions [3–5] offers a high cost reduction potential compared to PVD techniques as the material can be used more economically due to the direct patterning ability by printing processes and the handling under ambient pressure.

Most of the investigations concerning ITO nanoparticles were conducted on glass substrates as the coatings have to be annealed at high temperatures to improve the electrical conductivity. There are just a few investigations of ITO nanoparticle coatings on flexible polymer substrates described in the literature although flexibility becomes more and more important for applications.

Al-Dahoudi et al. [6] investigated coatings of ITO nanoparticles modified with the UV-curing binders 3-glycidoxypropyltrimethoxysilane (GPTS) or 3-methacryloxy-propyltrimethoxysilane (MPTS). Polymethylmethacrylate (PMMA) and polycarbonate (PC) substrates were coated by spin, dip and spray processes. Specific resistances of 0.25 Ω cm were achieved for a layer thickness of 570 nm by using UV-irradiation followed by a low temperature heat treatment under air and a reducing atmosphere at 130 °C. Puetz et al. [7] described a low temperature curing technique for coatings of ITO nanoparticles on PMMA, PC and PET substrates using UV-irradiation as well. MPTS together with a UV-photostarter was added to the dispersion. Specific resistances of 0.1 Ω cm were reached after a post-treatment in reducing atmosphere. As substrate materials PMMA, PC and different polyesters were used. In a further work, Puetz and Aegerter [8] investigated the fabrication of transparent conductive

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ITO nanoparticle coatings based on the modified ITO nanoparticle dispersion described above using direct gravure printing of PEN and PET substrates.

The stability of the electrical conductivity of ITO nanoparticle coatings under bending which is an essential property for the use in flexible applications is rarely described in the literature. Königer and Münstedt [9] studied the stability of the electrical conductivity of ITO nanoparticle coatings and commercial sputtered ITO coatings under oscillatory bending. The ITO nanoparticle coatings showed a significant higher stability of the electrical conductivity under oscillatory bending compared to the commercial sputtered ITO coatings.

In this work, ITO/PVP nanocomposites on flexible PET substrates were characterized with respect to their electrical conductivity and transparency. The intention of the use of the organic PVP as a film agent was to improve the stability of the electrical conductivity of ITO nanoparticle coatings under oscillatory bending.

It is already known that high-quality nanocomposite films based on SiO_2-, TiO_2- ZnO- or ITO-nanoparticles can be fabricated using the organic film agent PVP [10–13]. PVP improves the film formation and can thermally be crosslinked [14] yielding a composite with outstanding thermal stability and high mechanical strength. The low light scattering due to the amorphous structure makes it an ideal polymer for composite materials in optical applications.

However, the influence of PVP on the electrical conductivity and the stability of the electrical conductivity under oscillatory bending of ITO nanoparticle coatings were not yet investigated.

Experimental

Materials

As substrate material the polyester film Hostaphan GN 96 4600 with a film thickness of 96 μm was chosen. The PET film offers a high-dimensional stability which is required for printable electronic applications. Furthermore, the surface is very smooth leading to homogeneous coatings [9].

An ethanolic dispersion of ITO nanoparticles from Evonik Degussa GmbH with a solid content of 35.5 wt% was used as coating solution. The primary nanoparticles exhibit a diameter of 10–30 nm.

Different amounts of polyvinylpyrrolidone PVP K30 from BASF with a molar mass of ~50 kg/mol were added to the ethanolic dispersion of ITO nanoparticles and stirred for 1 h at room temperature. The PVP dissolved homogeneously in the ethanolic ITO nanoparticle dispersion and did not change the arithmetic mean value of the volumetric grain size distribution of ~100 nm which was measured by means of dynamic light scattering.

Film preparation

At first, the PET films were treated by plasma to improve the wettability. The plasma treatment was carried out for 30 s under air.

Afterwards, the polymer substrates were coated by means of doctor blading using an Erichsen Coatmaster 509 MC. Coil blades with a wet thickness of 30–100 μm dependent on the PVP content were used to achieve a dry thickness of 4 μm. The PET film was fixed to a heatable glass plate. The speed of the coil blade was set to 10 mm/s and the plate was heated up to 60 °C to get a quick evaporation of the ethanol. Under these conditions, a homogeneous coating was obtained.

The ITO/PVP nanocomposites were annealed at 200 °C for 20 min in air using a circulating air oven. The annealing parameters were optimized in former investigations.

Film characterization

The morphology of the ITO nanoparticle films was characterized using the scanning electron microscope FE-SEM S4800 from Hitachi.

The layer thickness of the coatings was determined by means of white light confocal (WL-CF) microscopy using the WL-CF microscope μsurf from Nanofocus.

The sheet resistance of the coatings was measured using the four-point method setup of a Keithley SMU 236. The specific resistance was calculated multiplying the sheet resistance by the layer thickness determined.

The transmission of visible light (400–800 nm) was measured using the spectrometer Lambda 19 from Perkin Elmer.

Electrical conductivity under oscillatory bending

The stability of the electrical conductivity of the coatings under bending was investigated using a new apparatus described in detail by Königer and Münstedt [15]. The device makes it possible to measure the electrical resistance of conductive coatings under oscillatory bending. In this work, the application of tensile stresses within the coating (Fig. 1) was used for the investigation of the electrical conductivity of the ITO/PVP coatings under oscillatory bending.

The polymer film is supported by four reels and flexibly fixed at its position by two springs on each side. The middle of the film sample is bent by a mandrel which can move up and down. The mandrel is mounted on a bar which is driven by an extender. The sample is bent around

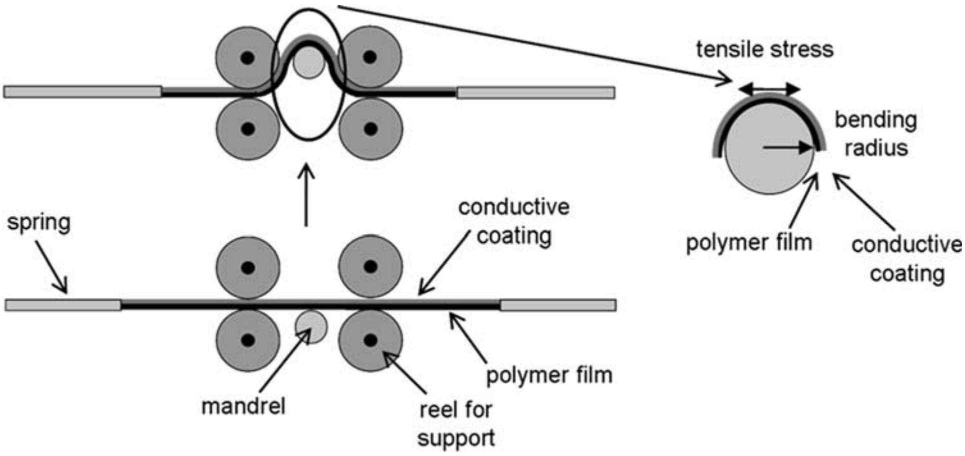


Fig. 1 Mode for the application of oscillatory tensile stresses

the mandrel, thus the bending radius is defined by the radius of the mandrel. The bending amplitude which defines the strength of the bending can be set by the displacement of the extender. The number of revolutions of the extender controls the frequency of the oscillatory bending load. The electrical contact between the conductive coating and the electrical measuring device is achieved by a conductive adhesive copper tape to which the wires from the ohmmeter are soldered.

For all measurements in this work, a frequency of 0.1 Hz was chosen and the bending amplitude was set to 20 mm which ensures a complete bending around the mandrel.

Results and discussion

Morphology of ITO/PVP nanocomposites

The influence of the organic film agent PVP on the morphology of ITO nanoparticle coatings was observed using FE-SEM. In Fig. 2, the morphology of an ITO/PVP nanocomposite coating with a PVP content of 40 vol.% is displayed.

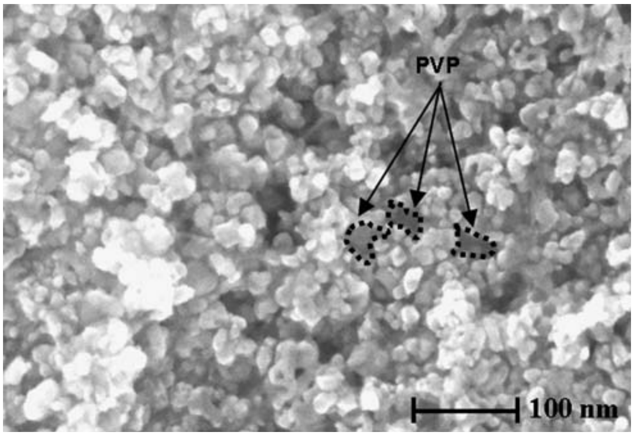


Fig. 2 Morphology of an ITO/PVP nanocomposite coating (40 vol.% PVP)

The investigations showed that the formation of the ITO nanoparticle network is not disturbed up to a PVP content of 40 vol.% which can be explained as follows.

It can be assumed that the PVP does not occupy the space between the ITO nanoparticles as the gyration radius of the PVP molecules is larger (approx. 40 nm [16]) than the diameters of the ITO nanoparticles between 10 and 30 nm. However, the PVP can fill the free space of the porous ITO nanoparticle coating up to a PVP content of 40 vol.% (Fig. 2) given by the porosity (40–45% [17]) of the ITO-coating. For PVP contents of more than 40 vol.%, the formation of the ITO nanoparticles network is hindered as the amount of PVP is higher than the porosity of the ITO nanoparticle coating.

Influence of PVP on the electrical conductivity

The nonconducting PVP has a strong influence on the electrical conductivity of ITO nanoparticle coatings. In Fig. 3, the specific resistance of ITO/PVP nanocomposites is plotted as a function of the PVP content.

Surprisingly, a strong decrease of the specific resistance was observed with growing PVP content up to 40 vol.%. For PVP contents of 33–40 vol.%, the lowest specific resistance of 6 Ω cm was measured which is about 20 times less than the specific resistance of pure ITO nanoparticle coatings. For PVP contents of more than 40 vol.%, the specific resistance increases as a result of the disturbed formation of the ITO nanoparticle network.

The decrease of the specific resistance with increasing PVP content can be attributed to a densification of the ITO nanoparticle network due to the shrinkage of PVP resulting from the evaporation of the solvent. This effect is described several times in the literature [10, 11]. The shrinkage of PVP creates compression forces between the ITO nanoparticles which can improve the contact of the ITO

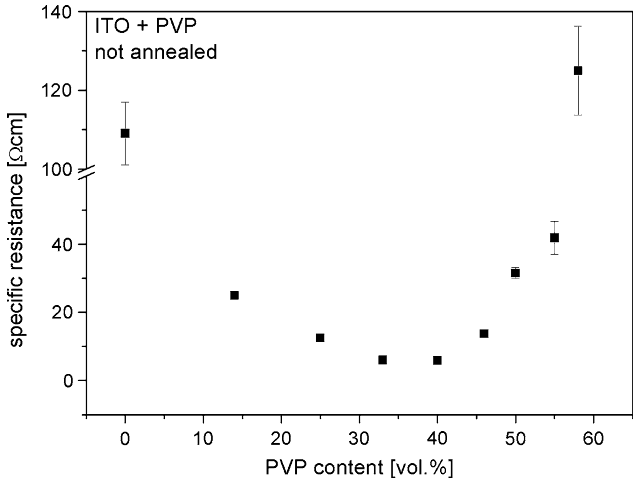


Fig. 3 Specific resistance of ITO/PVP nanocomposites as a function of the PVP content

nanoparticles. The better contact of the ITO nanoparticles enhances the charge carrier mobility and thus lowers the electrical resistance.

This effect led to the idea to improve the electrical conductivity further by annealing the ITO/PVP coating as PVP crosslinks at temperatures above 150 °C [10–12]. As it is well known, crosslinking creates additional shrinkage forces. They can cause a further densification of the ITO nanoparticle network and thus an improvement of the electrical conductivity.

The ITO/PVP nanocomposites were annealed at 200 °C, which is the maximum annealing temperature applicable to PET substrates. In Fig. 4, the specific resistance of annealed ITO/PVP nanocomposites is displayed as a function of the PVP content.

For all PVP contents, a distinct decrease of the specific resistance was observed after annealing at 200 °C. ITO/PVP nanocomposites with PVP contents of 33–40 vol.% show the lowest specific resistance of 0.5 Ω cm, which is 12 times lower than the specific resistance before annealing. For volume fractions of PVP of more than 40 vol.%, the specific resistance increases due to the disturbed formation of the ITO-nanoparticle network as explained above.

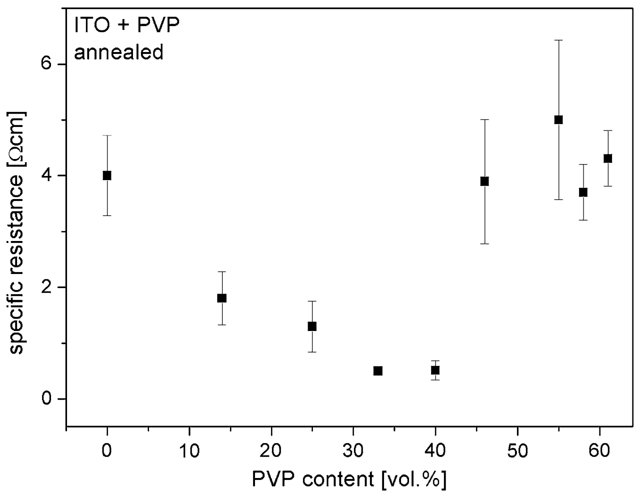


Fig. 4 Specific resistance of annealed (200 °C, 20 min) ITO/PVP nanocomposites as a function of the PVP content

For the confirmation of a further densification of the ITO/PVP nanocomposites by annealing at 200 °C, first the crosslinking behaviour of PVP was investigated by exposition to ethanol. For annealing temperatures up to 180 °C over 20 min, the PVP is completely soluble in ethanol after 1 h. In contrast, PVP films annealed at 200 °C for 20 min exhibit no weight loss within the accuracy of the measurement. Moreover, a strong swelling of the PVP occurs during soaking which indicates a thermally induced crosslinking at temperatures around 200 °C. Furthermore, dynamic mechanical measurements (DMA) were conducted which show a strong increase of the storage modulus at a temperature of 200 °C additionally confirming the crosslinking of PVP. The crosslinking mechanism of PVP can be attributed to residual hydrogen peroxide which is used to polymerize PVP. It causes a radical reaction forming interpolymer chain bondings [14].

The improvement of the electrical conductivity by shrinkage forces due to crosslinking was investigated by measuring the electrical resistance of ITO nanoparticle coatings and ITO/PVP nanocomposite coatings at different annealing temperatures. As an example, in Fig. 5, the specific resistance of ITO nanoparticle coatings and ITO/PVP nanocomposite coatings (25 vol.% PVP) is plotted as a function of the annealing temperature.

For the ITO nanoparticle coatings, a slight decrease of the specific resistance with increasing annealing temperature

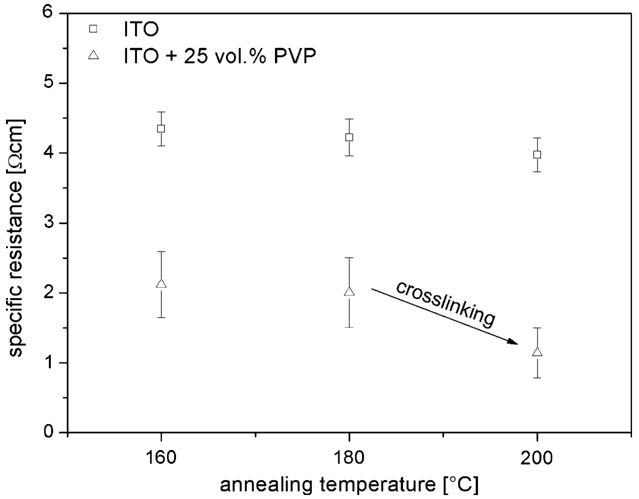


Fig. 5 Specific resistance as a function of the annealing temperature for ITO nanoparticle coatings and ITO/PVP nanocomposite coatings (annealing time 20 min)

was observed which can be attributed to the degradation of the electrically insulating organic dispersing agent covering the ITO particles in the dispersed not annealed state. Compared to the ITO nanoparticle coatings, the ITO/PVP nanocomposites show a distinct decline of the specific resistance between 180 and 200 °C affirming the assumption of a densification of the ITO nanoparticle network by the crosslinking of PVP at 200 °C.

Influence of PVP on the electrical conductivity under oscillatory bending

The aim of the modification of the ITO nanoparticle coating with the organic film agent PVP was to improve the stability of the electrical conductivity under oscillatory bending which is an essential requirement for flexible transparent electrodes.

In Fig. 6, the sheet resistance of annealed ITO nanoparticle coatings and annealed ITO/PVP coatings (40 vol.% PVP) is plotted as a function of bending cycles for a bending radius of 3 mm. The line with symbols represents the sheet resistance in the bent state. The dotted line represents the initial sheet resistance. As explained above, the ITO/PVP nanocomposites exhibit a lower initial sheet resistance due to the densification of the ITO nanoparticle network by the shrinkage of PVP after the ethanol evaporation. The ITO/PVP nanocomposite coating shows a distinct smaller increase of the sheet resistance under oscillatory bending compared to the ITO nanoparticle coating. For the ITO/PVP coating (40 vol.% PVP) an increase of just 750 Ω/□ from 1250 to 2000 Ω/□ was observed compared to an increase of 8000 Ω/□ for the ITO nanoparticle coatings starting from 8000 Ω/□. The lower increase of the sheet resistance can be explained by a less pronounced crack formation (Fig. 7).

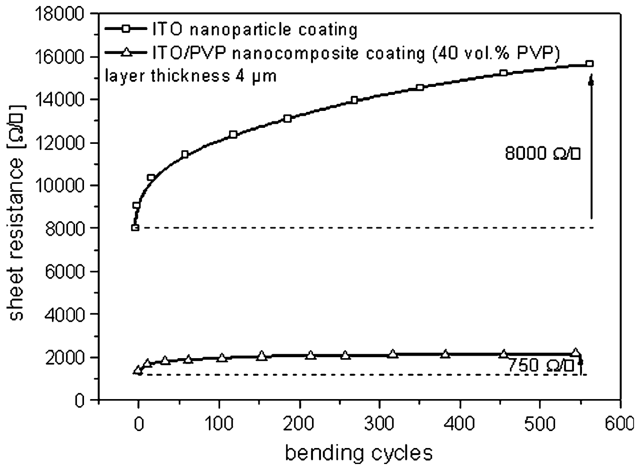


Fig. 6 Sheet resistance as a function of bending cycles (bending radius 3 mm, bending amplitude 20 mm) for an annealed (200 °C, 20 min) ITO nanoparticle coating and an annealed (200 °C, 20 min) ITO/PVP coating (40 vol.% PVP)

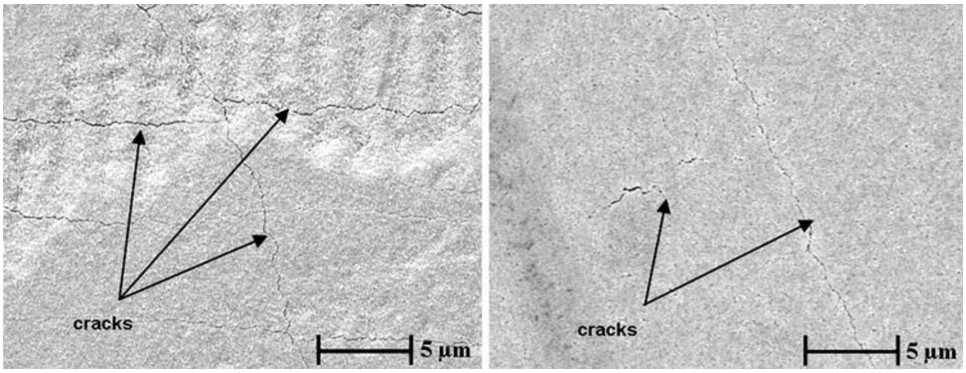
The organic film agent PVP, which fills the free space in the porous ITO nanoparticle coating, presumably acts as "elastic glue" and thus improves the elasticity of the coating. The higher elasticity of the coatings leads to a less pronounced crack formation.

The increase of the sheet resistance under oscillatory bending was investigated for different volume fractions of PVP. In Fig. 8, the increase of the sheet resistance in the bent state after 500 bending cycles (bending radius 3 mm) is plotted as a function of the PVP content.

A declining increase of the sheet resistance in the bent state after 500 bending cycles was observed with growing volume fraction of PVP up to 40 vol.%. For higher PVP contents (>50 vol.%), a significant increase of the sheet resistance was found.

These results can be explained in the following way. The higher the PVP content the more space of the porous ITO nanoparticle coating is filled with PVP which improves the elasticity of the coating and, therefore, lowers the crack formation. For PVP contents of more than 40 vol.%, some of the conductive paths formed by the ITO particles may be interrupted as shown by the smaller conductivity found (Fig. 4). This smaller number of continuous paths makes the conductivity of the system more susceptible to crack formation.

Fig. 7 Crack formation in annealed (200 °C, 20 min) ITO nanoparticle coatings (*left*) and annealed (200 °C, 20 min) ITO/PVP coatings (*right*, 40 vol.% PVP) after oscillatory bending (bending radius 3 mm, bending amplitude 20 mm, bending cycles 500)



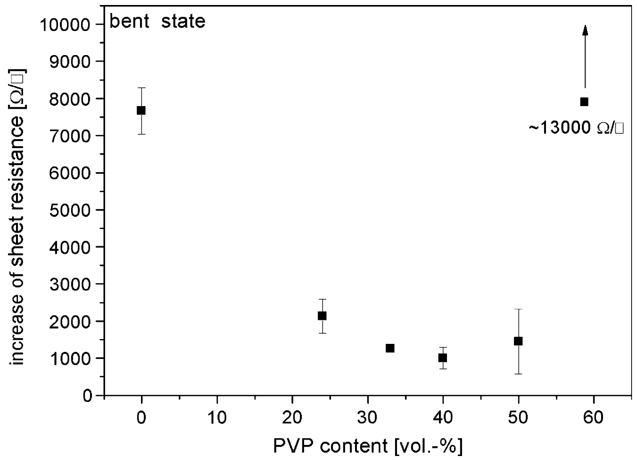


Fig. 8 Increase of the sheet resistance in the bent state after 500 bending cycles as a function of the PVP content (bending radius 3 mm, bending amplitude 20 mm)

Transmission in the visible range

With regard to the application of ITO/PVP coatings as transparent electrodes, the influence of the PVP content on the transmission of ITO/PVP nanocomposites in the visible range was investigated. In Fig. 9, the transmission in the visible range is displayed for different PVP contents.

A strong decrease of the transmission in the visible range was observed for PVP contents up to 40 vol.%. ITO/PVP coatings with a PVP content of 40 vol.% which exhibit the lowest specific resistance of 0.5 Ω cm show a transmission of just 50% at 550 nm for a layer thickness of 4 μm.

The decrease of the transmission in the visible range with growing PVP content up to 40 vol.% can be explained by two effects. First, the densification of the ITO nanoparticle network and the different refractive indices of ITO and PVP [13] lead to a stronger scattering of incident light. Second, a slight degradation of PVP after annealing at 200 °C [14] causes a yellow tint explaining the low transmission values for wave lengths ranging from 380 to 550 nm.

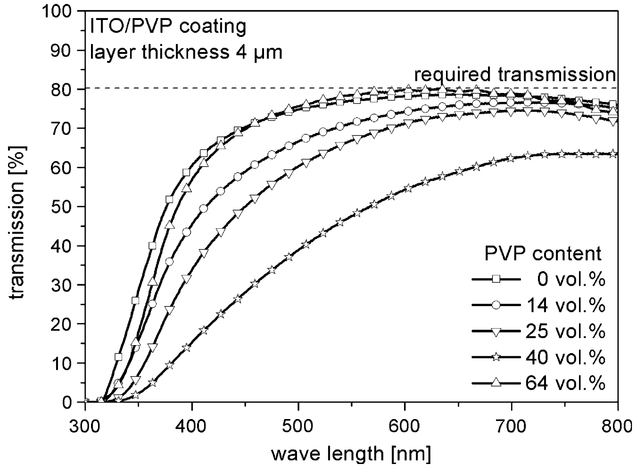


Fig. 9 Transmission in the visible range of ITO/PVP coatings on a PET film (96 μm) for different PVP contents

For PVP contents of more than 40 vol.%, the transmission in the visible range increases again due to fewer scattering centres in the more widely meshed ITO nanoparticle network.

Conclusion

The organic film agent polyvinylpyrrolidone has a strong influence on the electrical resistance of ITO nanoparticle coatings. The electrical conductivity of ITO nanoparticles increases with growing volume fraction of PVP up to 40% which can be explained by a densification of the ITO nanoparticle network due to the shrinkage of PVP caused by the evaporation of the solvent. The shrinkage forces improve the contact between the ITO nanoparticles and thus heighten the electrical conductivity. For a PVP content of 40 vol.%, the lowest specific resistance of 6 Ω cm was achieved which is about 20 times lower than the specific resistance of ITO nanoparticle coatings without PVP. For volume fractions of more than 40 vol.%, the formation of the ITO nanoparticle network is hindered by the PVP molecules leading to a significant decrease of the electrical resistance.

A further improvement of the electrical conductivity was achieved by annealing the ITO/PVP coatings at 200 °C. For a PVP content of 33–40 vol.%, the lowest specific resistance of 0.5 Ω cm was measured which corresponds to a sheet resistance of 1250 Ω/□ for a layer thickness of 4 μm. The improvement of the electrical conductivity after annealing is related to a further densification of the ITO nanoparticle network by crosslinking of PVP at 200 °C which creates additional shrinkage forces.

In addition, PVP improves the stability of the electrical conductivity of ITO nanoparticle coatings under oscillatory bending. ITO/PVP nanocomposites show a much lower increase of the electrical resistance under bending compared to a purely ITO nanoparticle coatings. The PVP reduces the crack formation which is probably due to the effect of PVP acting as “elastic glue” between the ITO nanoparticles and improving the elasticity of the coating.

Besides the electrical conductivity, the transmission in the visible range is significantly influenced by the PVP content. The transparency decreases up to a volume fraction of 40%. This behaviour can mainly be explained by a growing scattering of the incident light due to the densification of the ITO nanoparticle network and different refractive indices of PVP and ITO.

The investigations show that the organic film agent PVP has a strong influence on the electrical and optical properties of ITO nanoparticle coatings on a flexible PET substrate. PVP improves the electrical conductivity as well as its stability under oscillatory bending but worsens the transmission in the visible range.

Acknowledgements The project was performed within the research training group "Disperse Systems for Electronic Applications" in cooperation with the Evonik Degussa GmbH. The authors want to thank the German Research Foundation for the financial support, the Evonik Degussa GmbH for providing the ITO nanoparticle dispersion and Mitsubishi Polyester Films for the PET films.

References

1. Ray S, Banerjee R, Basu N, Batabyal AK, Barua AK (1983) J Appl Phys 54:3497
2. Hamberg I, Granqvist CG (1986) J Appl Phys 60(11):R123
3. Al-Dahoudi N, Aegerter MA (2006) Thin Solid Films 502:193
4. Ederth J, Heszler P, Hultåker A, Niklasson GA, Granqvist CG (2003) Thin Solid Films 445:199
5. Goebbert C, Nonninger R, Aegerter MA, Schmidt H (1999) Thin Solid Films 351:79
6. Al-Dahoudi N, Bisht H, Göbert C, Krajewski T, Aegerter MA (2001) Thin Solid Films 392:299
7. Puetz J, Al-Dahoudi N, Aegerter MA (2004) Adv Eng Mater 6(9):733
8. Puetz J, Aegerter MA (2008) Thin Solid Films 516(14):4495
9. Königer T, Münstedt H (2008) J Soc Inform Display 16(4):559
10. Yoshida M, Prasad PN (1996) Appl Optics 35(9):1500
11. Zheng M-P, Jin Y-P, Jinin G-l, Gu M-Y (2000) J Mater Sci Lett 19:433
12. Du T, Song H, Ilegbusi OJ (2007) J Mater Sci Eng C27:414
13. Carotenuto G, Valente M, Scimue G, Valente T, Pepe G, Ruotolo A, Nicolais L (2006) J Mater Sci 41:5587. doi:10.1007/S10853-006-0253-y
14. Scheirs J, Biggers W, Then ETH, Billingham NC (1993) J Polym Sci B Polym Phys 31:287
15. Königer T, Münstedt H (2008) Measure Sci Technol 19:055709
16. Sato T, Sato A, Arai T (1998) Colloid Surf A Physicochem Eng Aspect 142:117
17. Gross M, Winnacker A, Wellmann PJ (2007) Thin Solid Films 515(24):8567