JOURNAL OF MATERIALS SCIENCE 40 (2005) 569–574

Hardener type as critical parameter for the electrical properties of epoxy resin/polyaniline blends

P. TSOTRA*, K. G. GATOS, O. GRYSHCHUK, K. FRIEDRICH
Institut für Verbundwerkstoffe GmbH, Technische Universität Kaiserslautern,
Erwin-Schrödinger-Straße, 67663 Kaiserslautern, Germany
E-mail: panagiota.tsotra@ivw.uni-kl.de

Epoxy resin/polyaniline-salt (EP/PANI-DBSA) blends were prepared and cured with different types of hardeners. The effect of hardener type on the volume resistivity of the blends was investigated. It was found out that acidic curing agents support the conductive character of polyaniline, while alkaline hardeners conflict this property. Moreover, colour changes of the mixtures after the addition of the hardener revealed possible transformation of the conductive PANI-DBSA salt to the nonconductive PANI base form. An UV-vis analysis confirmed these assumptions. Despite of the acidic character of the anhydride type hardener, low conductivity was obtained. This was related to its insufficient curing action in the presence of PANI-DBSA. Furthermore, IR spectra of EP/PANI-DBSA blends varying the hardener type and the wt% of PANI-salt ($<$10 wt%) were recorded. These indicate a possible connection of the shoulder creation at the 1585 cm^{-1} band, spectral region 1575 to 1560 cm^{-1}, with the degree of volume resistivity.

1. Introduction

Intrinsically conductive polymers (ICPs) have attracted plenty of attention during the recent years, since they can be employed in a variety of applications, such as semiconductor devices, light-emitting diodes, antistatic coatings, and batteries [1]. Polyaniline (PANI) is definitely one of the most intensively investigated ICPs. In contrast to the *n*- and *p*-type doping processes applied to other conductive polymers, the emeraldine base (EB) form of polyaniline can be rendered conductive by a non-redox process [2–4]. In this protonation process, EB is treated with a protonic acid, e.g., dodecylbenzene sulfonic acid (DBSA) or camphor sulfonic acid (CSA), resulting in the emeraldine salt (ES). During the protonation process no addition or removal of electrons takes place, but enhancement of conductivity is achieved by an internal redox reaction.

The blends of polyaniline with other polymers have become a very interesting field of research, since polyaniline itself has very poor mechanical properties. Polymer blends with good mechanical and electrical properties can be developed in this way [5]. Peltola *et al.* [6] prepared electrically conductive epoxy adhesives based on PANI-CSA, which showed conductivities in the antistatic range (10^{-8}–10^{-3} S/cm) with less than 2 wt% of the conductive salt. Aiming to similar results, i.e., electrically conductive thermoset compositions, some researchers have directly mixed epoxy resin and polyaniline protonated with different acids, such as *p*-toluenesulfonate (PTSA), and DBSA [7–9]. The percolation values in these cases were at concentrations above 15 wt% of the conductive polyaniline salt.

The present paper describes the preparation and characterization of epoxy/polyaniline blends. To cure the blends, four different types of hardeners were used in order to investigate their effect on the final electrical properties.

2. Experimental

The thermosetting resin used was a bisphenol F epichlorohydrin epoxy resin (Epikote 862, Resolution Performance Products, The Netherlands). Four different hardeners were used to cure the resin (Fig. 1). Their properties are summarized in Table I. The amine and imidazole hardeners fall into the class of alkaline curing agents, while anhydride and BF_3 are of acidic type. For the initiation of the polymerization process in the case of anhydride hardener a catalyst was added (1-Methylimidazole, DY 070, Ciba-Geigy Ltd.) in approximately 0.5 phr EP. The pH value of this catalyst was ca. 9. The conductive salt used was polyaniline doped with DBSA (Panipol F, Panipol Ltd., Finland). The moral ratio of DBSA to PANI unit (PhN) is approximately equal to 1.1. This conductive salt exhibits an

---

*Author to whom all correspondence should be addressed.

0022–2461 © *2005 Springer Science + Business Media, Inc.*

TABLE I Characteristics of the different hardener types used

Designation	Amine	Imidazole	Anhydride	BF_3
Brand name	HY 2954	EMI-24	HY 917	ANCHOR 1170
Producer	Vantico	Air Products	Ciba	Air Products
Composition	Cycloaliphatic amine[a]	2-ethlyl-4-methylimidazole	MTHPA[b]	Trifluoroboron (4-chlorobenzeneamine)
Mixing ratio (phr EP)	35	4.4	90	10
Cure schedule (h/°C)	1/80; 4/120	3/60; 1/70; 1/100	4/80; 2/140	1/50; 2/70; 0.5/130
Density (g/cm^3)	0.94–0.95	0.99	1.20	1.25
pH (at 20°C)	12	11.5	3.7	3.8

[a] 2,2'-dimethyl-4,4'-methylene-bis(cyclohexylamine).

[b] Methyl-Tetrahydrophthalic Anhydride.

electrical conductivity of around 1 S/cm as a pressed pellet and has a pH value of 2–3.

PANI-DBSA was mixed with toluene, so as to create a 5% solution in it, and they were mixed together with a magnetic stirrer for 48 h. In order to improve the mixture's quality, this was treated in a ultrasonic bath for about 3 h and at the end a green transparent low-viscosity polymer solution was obtained. This solution was then mixed with the epoxy resin in a dissolver (Dispermat AE, VMA-Getzmann GmbH, Germany) under vacuum at 50°C, until the whole toluene was evaporated from the blend. The hardener was finally added and mixed at room temperature for 10 min. The mixing ratios and curing schedules for each type of hardener are shown in Table I, while their structures are illustrated in Fig. 1. Following this procedure, blends with 6.5 wt% PANI-DBSA were prepared. The curing process of the blends was investigated by differential scanning calorimetry (DSC 821 device, Mettler Toledo) in the presence of nitrogen. Uncured samples were heated up to 250°C, with a heating rate of 10°C/min. The total heat of the reaction (ΔH) was estimated by drawing a straight line connecting the baseline before and after the peak, and integrating the area under the peak.

Volume resistivity measurements of the cured samples were conducted using a Hiresta UP high resistivity meter (Mitsubishi Chemicals, Japan). A direct current voltage of 10 V was applied across the sample thickness (2 mm) when the resistance of the sample was less than 10^8 Ω, while for higher resistances voltages up to 1000 V were applied. The samples were dried over night in an oven at 40°C under vacuum (in order to remove any residual water and solvent), and then stored in a desiccator. Furthermore, the two surfaces of the samples were coated with conductive paint to reduce the contact resistance.

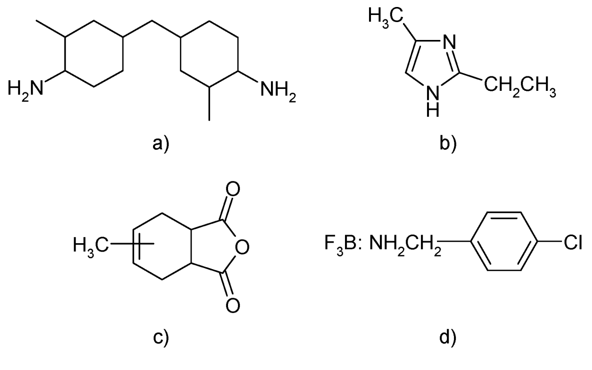


Figure 1 Chemical structures of the different types of curing agents: (a) amine, (b) imidazole, (c) anhydride, and (d) BF_3.

The pH values of the different hardeners, as well as of the polymer blends before curing, were measured by a pH electrode (SenTix 81, WTW) in connection with a measuring system (inoLab Level 3, WTW) at room temperature.

UV-transmission spectra of the polymer blends were recorded at room temperature on a UV-vis scanning spectrophotometer (UV-2101PC, Shimadzu). Dilute solutions of the polymer samples in toluene were used. Spectra of PANI-EB and the PANI-DBSA were also measured for comparison. For the PANI-EB, N-methylpyrrolidone (NMP) was used as solvent and reference, whereas toluene for the doped polymer. The transmission spectra of the solutions were measured in a range between 800 and 300 nm.

Fourier transform infrared spectroscopic measurements (FTIR) were performed on a Nicolet 510 spectrometer (Madison, Wisconsin, USA). The cured blends were mixed in a powder form with KBr and pressed to disks. FTIR spectra were recorded in the transmission mode at 4 cm^{-1} spectral resolution (the minimum number of scans 32).

3. Results and discussion

3.1. Resistivity measurements

The values of the volume resistivity of EP/PANI-DBSA blends cured with each of the above described hardeners are shown in Table II. It can be observed that the blends cured with amine and imidazole exhibit very high values of volume resistivity (above the limit of the measuring device). In the case of anhydride, an enhancement of the conductivity is observed compared to that of the neat matrix, but the material remains in the insulating range. Nevertheless, the use of the BF_3 curing agent leads to a reduction in the volume resistivity by many orders of magnitude.

In order to study in more detail the system cured with BF_3, blends with various concentrations of

TABLE II Characteristics of the EP/PANI-DBSA blends mixed with different hardeners

	Amine	Imidazole	Anhydride	BF_3
Colour	Blue	Blue	Green	Green
pH (at R.T.)	10.5	9.5	4.5	1.6
ΔH (J/g)	361	422	57	410
Peak maximum (°C)	106	138	225	94
Peak start temperature (°C)	68	130	160	75
Peak end temperature [°C]	149	141	255	117
Volume resistivity after curing (Ω·cm)	$>10^{14}$	$>10^{14}$	3×10^{11}	2.3×10^4

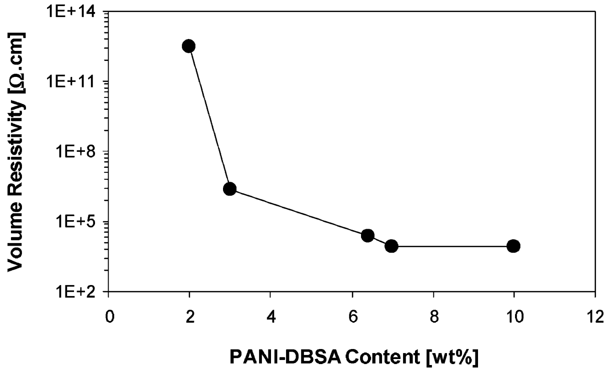


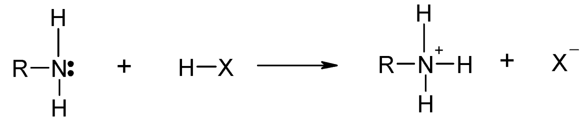
Figure 2 Volume resistivity versus PANI-DBSA content for blends cured with the BF_3 hardener.

PANI-DBSA (0–10 wt%) were prepared. The dependence of the volume resistivity values on the concentration of the conductive salt is presented in Fig. 2. A sharp decrease in volume resistivity is observed at a content of 3 wt% PANI-DBSA. When more PANI-DBSA is added, the volume resistivity is further reduced. No additional reduction in this value is evident for a content of 10 wt% PANI-DBSA.

In a further effort to investigate the parameters influencing the electrical properties of the EP/PANI-DBSA blends, samples were prepared without first dissolving the conductive salt in toluene but mixing it directly with the resin. For having as reference a blend with good electrical properties, these samples were cured with the BF_3 hardener. Since PANI-DBSA was not soluble in the EP matrix, finally a poor dispersion of the conductive salt was obtained. The volume resistivity measurements of such a blend containing 7 wt% PANI-DBSA showed that it was an insulator, in contrast to the blend with the same amount of PANI-DBSA produced via the solution procedure (Fig. 2). It is hence obvious that PANI-DBSA dispersion quality is closely related to the final electrical properties of the blends. A poor dispersion reflects the creation of agglomerates, which are mostly surrounded by the insulating matrix without being able to come in contact with each other. On the other hand, the enhanced distribution of the conductive salt, which is achieved by the use of toluene as a solvent, leads to a fine conductive network in the EP matrix. As a consequence, enhanced electrical properties are observed.

3.2. Optical observations

During the preparation of the blends changes in their colour were noticed after the addition of the hardener. Polyaniline in the protonated emeraldine form, like PANI-DBSA used here, has a dark green colour. Therefore, a green solution was obtained after mixing it with toluene. This colour remained after the addition of the resin. However, the colour of the blends changed from green to blue when the amine or the imidazole hardener was added. No colour changes were evident in the case of the anhydride and BF_3 curing agents. According to the literature [10], protonated emeraldine converts to the blue, nonconductive emeraldine base form upon direct treatment with bases. Chiang *et al.* [4] reported, for example, that emeraldine hydrochloride converts to the emeraldine base by stirring with a dilute aqueous methanolic solution of KOH. Amines have a basic character. The nitrogen atom of amine has a pair of electrons, and this gives rise to characteristics of nucleophilicity and basicity. The basic character of the amines can be schematically presented by the following reaction:



$$\mathrm{R{-}\ddot{N}H_2} + \mathrm{H{-}X} \longrightarrow \mathrm{R{-}\overset{+}{N}H_3} + \mathrm{X^-}$$

On the other hand, Sertova *et al.* [12] have presented the deprotonation of the PANI-HCl salt using a base by the following form:

$$\mathrm{PANI^+Cl^-} \xrightarrow[\text{base}]{\mathrm{R^+}} \mathrm{PANI(EB)} + \mathrm{RCl}$$

It is therefore possible that a reaction takes place between the dopant of PANI, in our case the DBSA, and the amine, which finally leads to deprotonation of the conductive salt.

From a similar point of view, several researchers have emphasized the importance of pH on the protonation state of PANI salts [1, 4]. As an example, highly conducting state of the PANI-hydrochloride salt can be obtained at low pH while a low conductivity state is achieved at a pH-value above 4. However, the sulfonated form of PANI can retain its conductivity up to pH 7 or 8. The pH-values of the blends before curing are shown in Table II. It can be observed that the blends with the higher pH-values, i.e., with amine and imidazole, are those who exhibit the higher values of volume resistivity after curing. In the same way, the blend cured with BF_3, having a strongly acidic character, has the highest electrical conductivity. Therefore, a strong connection is evident between the conductivity of the EP/PANI-DBSA blends and the colour and pH-values of the mixtures before curing. These properties seem to be strongly related to the type of hardener used.

3.3. UV-visible analysis

Fig. 3 shows the UV-spectra of PANI-EB and PANI-DBSA solutions. It should be noted that in this diagram

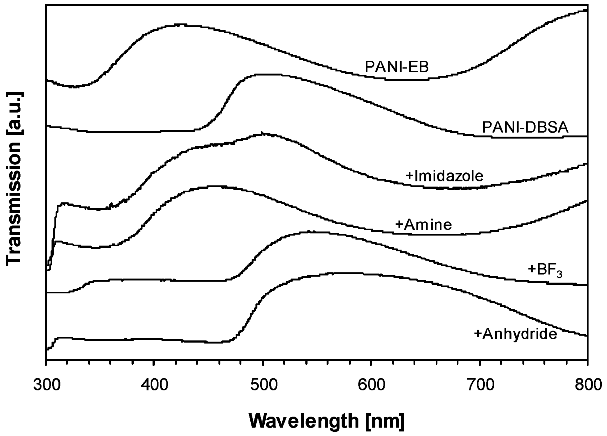


Figure 3 UV-vis spectra of PANI-EB, PANI-DBSA and EP/PANI-DBSA blends with different hardener types.

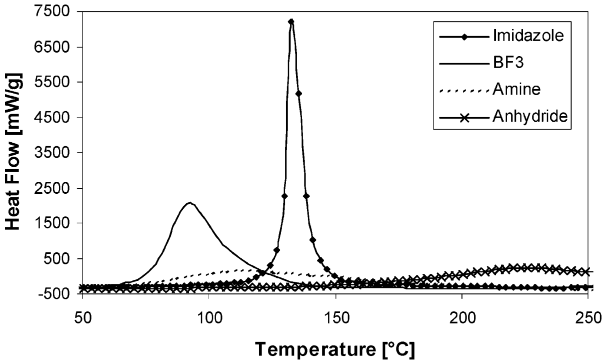


Figure 4 DSC thermograms of EP/PANI-PANI blends with different hardener types.

the transmission of the solutions is presented, and therefore, the minimum values of the curves represent the related peaks. The base polymer shows two characteristic peaks: at 330 nm due to a $\pi \rightarrow \pi^*$ transition of the benzenoid amine structure, and at 630 nm, corresponding to the excitation of the quinoid imine structure [13]. For the doped PANI-DBSA, the peak 630 nm disappears. This indicates that PANI is in a fully protonated state [11]. The position of the peak at 330 nm does not change, whereas two new peaks at 450 and 800 nm occur, both stemming from the formation of delocalized polarons [14]. The spectra of the EP/PANI-DBSA blend, cured with anhydride and BF_3, confirm the initial hypothesis that PANI-DBSA remained in the doped state, as evidenced by the characteristics peaks. In contrast, the spectra of the blend cured with amine and imidazole show the peaks corresponding to the nonconductive PANI-EB, which is in good agreement with their conductivity values.

An interesting observation of the above mentioned results is that the cured anhydride sample did not show enhanced electrical properties, although the UV-spectra of the blend exhibited peaks similar to those of PANI-DBSA. This may be closely related to the cured state of the final samples. The thermograms during the polymerization of the EP/PANI-DBSA blends with the various of curing agents are compared in Fig. 4. The DSC data, as summarized in Table II, show that the exotherm peaks for the systems with amine, imidazole, and BF_3 lay within their cure schedule (Table I), while for the system with anhydride the curing behavior is different. It is speculated that PANI-DBSA influences negatively the curing reaction of this system, leading to a poor cross-linked network with poor electrical properties. Jia *et al.* [8] had also observed, by means of DSC analysis, a partial inhibition of the cross-linking reaction of epoxy groups with anhydride groups due to the presence of DBSA.

3.4. FTIR analysis

The type of the hardener used, as well as the concentration of PANI-DBSA in the blend, was found to be crucial for the good electrical properties of the final material. Considering the fact that the Fourier transform infrared spectroscopy (FTIR) is capable of supplying information from macromolecular level, the study of the FTIR spectra can be useful for the conductivity determination.

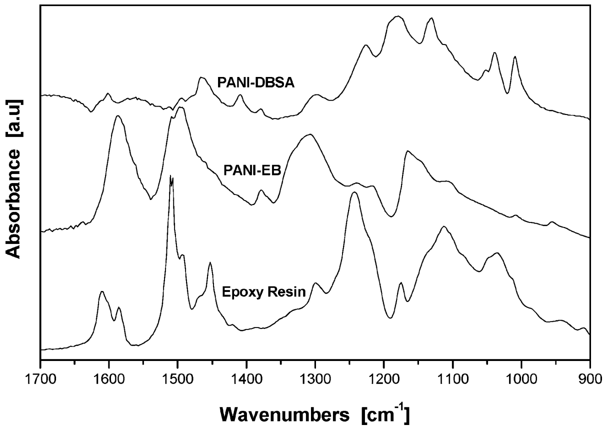


Figure 5 FTIR spectra of PANI-EB, PANI-DBSA and epoxy resin with BF_3 hardener.

Peaks in the FTIR spectrum of the PANI that arise upon the doping procedure have already been presented, and several peaks have been assigned. Nevertheless, few spectroscopic analyses are correlated with the degree of conductivity [15, 16]. Sariciftci *et al.* [15] studied the oxidation process of polyaniline using FTIR and reported the appearance of a broad absorption band centred at about 4000 cm^{-1} for the intermediate oxidized metallic form of PANI. In the current analysis the PANI was received in its semi-oxidized form, in which we believe that remained during the treatment with the different hardener types.

Fig. 5 depicts the spectra of PANI, PANI-DBSA and epoxy resin when BF_3 was used as a hardener. The absorption bands at 1586 and 1496 cm^{-1} for the PANI base are attributed to the C=C stretching vibration of the quinoid and the benzenoid ring, respectively [17, 18]. The DBSA in the doped PANI is detected at the bands 1038 and 1009 cm^{-1} which are assigned to the S=O stretching vibrations [19, 20]. The bands at 1600 and 1500 cm^{-1} region for the epoxy resin cured with BF_3 (Fig. 5) are attributed to the benzene ring vibrations [21, 22]. As shown in Fig. 5, in the absorption region between 1650 and 1500 cm^{-1}, PANI-DBSA presents a distinct peak at 1601 cm^{-1} and a broad band around 1565 cm^{-1}. In this latter area, the N-H deformation vibrations (in plane) have been mentioned to absorb very weakly, which makes them difficult to be identified [23].

In Fig. 6a, the spectra of the EP/PANI-DBSA blends cured with BF_3, at different concentrations of PANI-salt, are presented for the spectral region between 1730 and 1400 cm^{-1}. A closer view in the region from 1600 to 1550 cm^{-1} for samples with 7 and 10 wt% PANI-DBSA can reveal the appearance of a broad shoulder on the 1585 cm^{-1} peak (indicated by an arrow). This is in the range of 1575 to 1560 cm^{-1}. Having in mind that the conductivity measurements showed a sharp increase after 3 wt% PANI-DBSA, a relation between these two observations might be the case. The appearance of this shoulder can be likely assigned to the N-H deformation vibrations. The presence of the DBSA can affect the environment of this vibration. From the

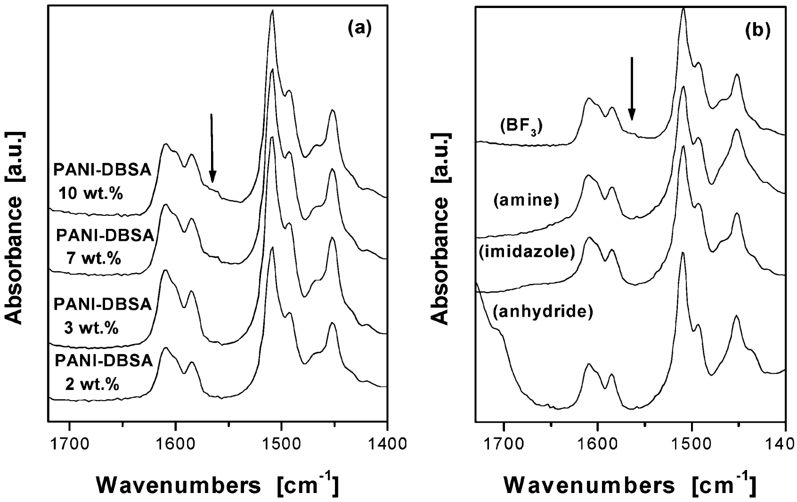


Figure 6 FT-IR spectra of (a) different PANI-DBSA percentages in the epoxy matrix using BF_3 as curing agent, and (b) blends containing 6.5 wt% of PANI-DBSA cured with different hardener types.

theoretical point of view, the interaction between the N-H of PANI and the DBSA (protonation) is responsible for the polaron creation and the degree of conductivity. As the material becomes conductive, the vibration is being altered. Considering the weak absorption in this region, the spectra in the figures are as recorded without any baseline correction that could wrongly estimate the image of the spectra. Peak shoulder creation increasing PANI-salt content has been reported for poly(N,N-dimethylacryl-amide) (PDMA) blended with PANI-PSA or PANI-SSA (PANI doped with p-phenolsulfonic acid or 5-sulfo-salicylic acid, respectively) [24]. In that case, the peak-shift to lower wave numbers for the carbonyl band of PDMA at 1644 cm^{-1} was attributed to the hydrogen bonding of the respective group with the PANI-salts.

Using amine or imidazole as a curing agent for the epoxy resin results in non-conductive blends. Similar results were also performed when anhydride was served as a hardener (Table II). As shown in Fig. 5b, it is interesting to observe that the shoulder, which is detected in the region of 1575 to 1560 cm^{-1} in the case of BF_3 hardener, is missing when amine, imidazole or anhydride with the same amount of PANI-DBSA (6.5 wt%) are used. Thus, it is speculated that the increase of the absorbance in the above-mentioned spectral region (as presented in Fig. 5a), is not only related to the higher amount of PANI-DBSA in the blend, but moreover with the different action of the hardener types on the emeraldine salt and consequently, with the volume resistivity of the blends.

4. Conclusions

The influence of the hardener type on the electrical properties of EP/PANI-DBSA blends was investigated. The volume resistivity measurements of the samples showed significant differences when an alkaline or an acid hardener was used for curing the epoxy system. Samples cured with alkaline hardeners (i.e., amine or imidazole) showed very high values of resistivity, close to that of the insulating EP matrix, even at high PANI-DBSA contents. On the contrary, when the acidic curing agent (BF_3) was used, PANI-DBSA led to a drastic decrease in volume resistivity, which reached a value of 2×10^4 Ω·cm for 6.5 wt% PANI-DBSA. The optical observation throughout the mixing procedure showed that the colour of the blends changed from green to blue by the addition of alkaline hardeners, while in the case of BF_3 or anhydride no colour change was evident. This fact pointed out a PANI-DBSA to PANI-EB conversion when the alkaline hardeners were used, probably due to their basic character. UV-vis analysis confirmed these observations in the case of the alkaline and BF_3 curing agents. Furthermore, contradicting to the UV-vis results, curing with anhydride led to the creation of an insulating blend. This was attributed to the insufficient action of the anhydride hardener in the presence of the PANI-DBSA leading therefore to poor network development. The FTIR spectra recorded for EP/PANI-DBSA blends with varying hardener type and PANI-DBSA content revealed a possible connection of the appearance of a shoulder at the 1585 cm^{-1} band in the spectral region 1575 to 1560 cm^{-1} with the degree of volume resistivity. Finally, additionally to the hardener type used, the dispersion quality of PANI-DBSA proved to be crucial for the final electrical properties of the blends. Samples prepared without dissolving PANI-DBSA in toluene showed poor dispersion of the salt in the EP resin, and, moreover, high values of volume resistivity.

Acknowledgements

The authors are grateful to Prof. J. Karger-Kocsis and Dr. J. Hartikainen for the useful discussions and their valuable comments on this study. Further thanks we due to the German Research Foundation (DFG FR 675/35-2) for the financial support of this work.

References

1. R. H. FRIEND, *Rapra Rev. Rep.* **63** (1993) 1.
2. R. S. KOHLMAN, J. JOO and A. J. EPSTEIN, "Physical Properties of Polymers Handbook" (AIP Press, New York, 1996) p. 453.
3. A. G. MACDIARMID and A. J. EPSTEIN, *Mater. Res. Symp. Proc.* **328** (1994) 133.

4. J.-C. CHIANG, MACDIARMID, *Synth. Met.* **13** (1986) 193.
5. H. MORGAN, P. J. S. FOOT and N. W. BROOKS, *J. Mater. Sci.* **36** (2001) 5369.
6. J. PELTOLA and Y. CAO, *Adhesives Ages* **38** (1999) 18.
7. P. KATHIRGAMANATHAN, *Polymer* **34** (1993) 2907.
8. W. JIA, TSCHOUDAKOV, E. SEGAL, R. JOSEPH, M. NARKIS and A. SIEGMANN, *Synth. Met.* **132** (2003) 269.
9. P. TSOTRA and K. FRIEDRICH, *J. Polym. Mat.* **19** (2002) 389.
10. J. STEJSKAL, P. KRATOCHVIL and A. D. JENKINS, *Polymer* **37** (1996) 367.
11. M. WAN and J. YANG, *J. Appl. Pol. Sci.* **55** (1995) 399.
12. N. SERTOVA, B. GEFFROY, J.-M. NUNZI and I. PETKOV, *J. Photochem. Photobiol. A: Chem.* **113** (1998) 99.
13. W. S. HUANG and A. G. MACDIARMID, *Polymer* **34** (1993) 1833.
14. Y. XIA, J. M. WIESINGER, A. G. MACDIARMID and A. J. EPSTEIN, *Chem. Mater*. **7** (1995) 443.
15. N. S. SARICIFTCI, H. KUZMANY, H. NEUGEBAUER and A. NECKEL, *J. Chem. Phys.* **92** (1990) 4530.
16. H. KUZMANY, N. S. SARICIFTCI, H. NEUGEBAUER and A. NECKEL, *Phys. Rev. Lett.* **60** (1988) 212.
17. S. A. CHEN and H. T. LEE, *Macromolecules* **26** (1993) 3254.
18. M. G. HAN and S. S. IM, *J. Appl. Polym. Sci.* **71** (1999) 2169.
19. D. POUSSIN, H. MORGAN and P. JS. FOOT, *Polym. Int.* **52** (2003) 433.
20. J. HARTIKAINEN, M. LAHTINEN, M. TORKKELI, R. SERIMAA, J. VALKONEN, K. RISSANEN and O. IKKALA, *Macromolecules* **34** (2001) 7789.
21. N. B. COLTHUP, L. H. DALY and S. E. WIBERLEY, in “Introduction to Infrared and Raman Spectroscopy” (Academic Press, San Diego, 1990) p. 261.
22. T. JEEVANDA, S. PALANIAPPAN and SIDDARAMAIAH, *J. Appl. Polym. Sci.* **74** (1999) 3507.
23. M. AVRAM and GH. MATEESCU, in “Infrared Spectroscopy” (Wiley-Interscience, New York, 1972) p. 322.
24. S. H. GOH, H. S. O. CHAN and C. H. ONG, *J. Appl. Polym. Sci.* **68** (1998) 1839.

Received 24 September
and accepted 11 October 2004